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DEGREE FOR WHICH THESIS WAS PRESENTED

Master of Science

YEAR THIS DEGREE GRANTED

1980

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RETENTION OF ANTIOXIDANTS IN FREEZE-THAW POTATO GRANULES

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE
in
FOOD PROCESSING

DEPARTMENT OF FOOD SCIENCE

EDMONTON, ALBERTA

FALL, 1980

80F-137

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled RETENTION OF ANTIOXIDANTS IN FREEZE-THAW POTATO GRANULES submitted by Edgar Julio Segura Vaca in partial fulfilment of the requirements for the degree of Master of Science.

SUMMARY

A study was carried out to determine the retention of BHA and BHT in production of dehydrated potato granules by a freeze-thaw process. Retention of antioxidants was followed in mashing; pre- and final drying steps of the process. Retention of the antioxidants during storage of granules at 25 and 37°C in polyethylene bags for a period of six weeks was also investigated.

During potato granule production, three different methods of antioxidant application were assayed, i.e. addition in the forms of powder, emulsion and ethanol solution. Two different formulations of emulsion were used; one consisted of antioxidant, surfactant (Myvatex) and water, while the other included the addition of the surfactant Tween 60. No appreciable difference was detected between them with regard to antioxidant retention.

Application of antioxidants in powder form appeared to offer the highest retention of antioxidants by potato granules, while liquid form application increased their volatility, resulting in less retention. No appreciable difference in retention values was obtained between the two formulations of emulsions used. A high degree of correlation between the loss of moisture content and the

loss of antioxidant showed that the combined effect of steam distillation and volatilization is mainly responsible for the poor antioxidant retention in the potato granule end product with approximately 7% moisture. Lowering the temperature of predrying and drying steps from 85°C to 60°C and to 50°C resulted in even lower antioxidant retention. This could be ascribed to the fact that at a lower temperature a longer time was required to accomplish each step.

A storage test over a period of six weeks with dehydrated granules packed in polyethylene bags at both temperatures assayed showed a steady decline in antioxidant concentration. As expected, BHT had a lower retention than BHA due to the higher volatility of BHT. Differential pulse voltammetry was a highly satisfactory quantitative and qualitative method for simultaneous determination of BHA and BHT. The antioxidants were recovered from dehydrated granules by benzene extraction at room temperature, while distillation was used as an extraction method for the samples which had a moisture content higher than 30%, since the higher moisture content in mashed potatoes considerably reduced the extraction capacity of benzene. The benzene extraction procedure was rapid and efficient, and was favored by the fact that no pretreatment or separation procedures were required.

RESUMEN

El presente estudio se llevó a cabo para determinar la retención de BHA y BHT en la producción de gránulos de papa deshidratados, por el procedimiento de Congelación-descongelación. Se comprobó la retención de los antioxidantes durante las etapas de preparación del puré, pre-secado y secado del proceso. Tambien se investigó la retención de los antioxidantes durante almacenamiento de los gránulos a 25 y 37°C en bolsas de polietileno por un período de seis semanas.

Durante la producción de gránulos de papa, se utilizaron tres métodos diferentes para la aplicación de los antioxidantes, adición en forma de polvo, emulsión y solución alcoholica. Se utilizaron dos diferentes formulaciones de emulsion; una consistía de antioxidante, tensioactivo (Myvatex) y agua, la otra incluía la adición del agente tensioactivo Tween 60.

No se encontró ninguna apreciable diferencia entre ellas en cuanto a retención del antioxidante. La aplicación de los antioxidantes en forma de polvo paració ofrecer la mayor retención de ellos en los gránulos de papa, mientras que las formas de aplicación liquidas aumentaban su volatilidad, dando como resultado menos retención. No se encontraron diferencias apreciables en la retención

obtenida entre las dos formulaciones de emulsión utilizadas; el alto grado de correlación entre la pérdida del contenido de humedad y la pérdida del antioxidante, demostraron que el efecto combinado entre la destilación al vapor y la volatilización son principalmente los responsables de la baja retención de los antioxidantes en el producto final de los gránulos de papa, con un contenido de humedad aproximademente del 7%.

El reducir la temperatura de las etapas de presecado y secado de 85°C a 60°C y 50°C, dio como resultado aún mas baja retención de los antioxidantes, Esto se debe al hecho de que a menor temperatura se necesitó un período de tiempo mas largo para concluir cada paso.

La prueba de almacenamiento de los gránulos deshidratados empacados en bolsas de polietileno, durante un periodo de seis semanas, a las dos temperaturas utilizadas; mastró una permanente disminución en la concentración de los antioxidantes. Como se esperaba, BHT tuvo mas baja retención que BHA debido a la alta volatilidad del BHT.

El método de Voltametría diferencial de pulso, resultó ser un método altamente satisfactorio, tanto cualitativa como cuantitativamente para la determinación simultánea de BHA y BHT. Los antioxidantes se separaron de los gránulos deshidratados por extracción con benceno a temperatura ambiente, mientras que para las muestras con

un contenido de humedad mayor del 30% se utilizó la destilación como método de extracción; ya que el mayor contenido de humedad del puré de papa reduce considerablemente la capacidad extractiva del benceno.

El hecho de no necesitarse una separación o tratamiento previos, ayudó a que el procedimiento de extracción fuera rápido y eficiente.

ACKNOWLEDGEMENTS

This study could not have been undertaken without the guidance, patience and understanding of my supervisor, Dr. Buncha Ooraikul, to whom I express my sincere gratitude.

Appreciation is extended to Dr. Dimitri Hadziyev for his counsel, incredible love for research and encouragement in my disheartened moments.

To Dr. David Schroder for his serving as a committee member.

To Dr. H. Jackson, Canadian International Development Agency, the Food Science Department, the Alberta Potato Commission and the Alberta Agricultural Research Trust, for their financial support.

Special thanks are due to Len Steele for his technical assistance and great sense of humor in the organization of this manuscript.

Finally, I wish to give a special appreciation to F. L. - just because.

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1. INTRODUCTION

The potato is one of the most important vegetables world-wide. Methods have been developed to produce many products which are stable over a long period of time, and an ever increasing proportion of the crop is being processed. For example, in 1975 about 57% of the potatoes in the U.S.A. were used by processors, with 22% being used for dehydrated products (Smith, 1977).

Potatoes are dehydrated on a commercial scale into dices or "instant mashed potatoes" (flakes, or granules) which are widely used by consumer and institutional markets.

Potato flakes are produced by applying cooked mashed potatoes to the surface of a single drum dryer (Cording and Willard, 1956). The deposited layer of solids is dried to about 6-7% moisture in about 20 seconds. The dried sheets are then cut into small flakes suitable for packaging. Since the bulk density of the flakes is normally very low (approximately 0.35 g/cm^3), packaging and shipping costs of the product are relatively high. The low bulk density of flakes also makes it uneconomical for them to be packed under nitrogen to retard oxidative rancidity, therefore, antioxidants must be used to protect the product against oxidative deterioration during storage

(Feustel et al, 1964). Improvements have been made to minimize some of the problems encountered. Bulk density can be increased to about 0.77 g/cm^3 by forming flakelets (Eskew and Drazga, 1962). Flakelets are produced by mixing dried flakes with freshly sliced potatoes to give a much denser laminates and aggregates which are then dried on a vibrating bed dryer to the desired moisture content. Packaging under nitrogen to improve shelf life is economically feasible because of the higher bulk density of flakelets.

Potato granules are one of the most commercially successful dehydrated mashed potato products. They are dehydrated single cells or aggregates of cells, dried to about 6-7% moisture. The granules are readily reconstituted into mashed potatoes by mixing in hot water or milk. They are suitable for both home and institutional use, and can be reconstituted according to personal preference with a texture ranging from dry and mealy to moist and creamy. The high bulk density of the granules (0.85 g/cm^3 or higher) reduces costs of packaging, shipping and storage.

2. OBJECTIVES OF THE INVESTIGATION

One common problem with instant mashed potato products is the deterioration of flavor during shipping and storage due to oxidative rancidity involving potato lipids. Antioxidants such as BHT and BHA have been used to prolong shelf life by suppressing or retarding the onset of the autoxidative reaction. Much work has been done on the effect of antioxidants on the shelf life of flakes and granules produced with the commercial Add-Back (A-B) process. However, a major problem is the difficulty of ensuring adequate retention of the antioxidants in the product. The greatest loss of antioxidants takes place during processing, so various methods of application have been developed to reduce this loss. These include application of antioxidants in powder form, an emulsion or vegetable oil or ethanol solutions. Some methods appear to be reasonably effective for flakes, while some are better with the A-B granules.

Freeze-Thaw (F-T) potato granules, which were developed recently in this laboratory (Ooraikul, 1977), however, have not been investigated with respect to the effect of antioxidants on shelf life. The F-T process, which is quite different from the commercial A-B process, may respond differently to the various antioxidant application

techniques. Also, the fate of the antioxidants in the F-T granules during storage may differ from that in potato flakes or A-B granules. Therefore, this study was designed to provide information in these areas. The objectives of this investigation of F-T granules were to determine:

1. The effectiveness of application techniques for BHT and BHA with respect to antioxidant retention through various steps of the process.
2. The extent of loss of antioxidants during storage at ambient and elevated temperatures.

3. LITERATURE REVIEW

3.1 Potato Granule Production

Development of a dehydrated potato granule process started during the latter part of World War II as a project sponsored by the Subsistence Research and Development Laboratory of the United States Army Quartermaster Corps. The process was based essentially on the work of Barker and Burton (1944). In the same year a dry powder from which mashed potatoes could be prepared almost instantly was patented by Volpertas. The process involved predrying potato cubes in an environment of steam, applying a vacuum until 30-40% of the original weight was lost. The moist powder was cooled in an air stream until the water content was reduced to about 12-15%. Fresh potato mash was then added to the powder until the mixture was homogeneous. The mix was dried further under vigorous stirring to obtain the final product.

Since the dried particles had a hard skin unsuitable for fast reconstitution, Rendle (1945) suggested drying the product in stages under carefully controlled conditions of temperature. A special agitating device was used to mix the mash with an approximately equal weight of seed powder (coarse dry particles from any

previous batch) to decrease water content to 40-45% by weight.

The mixed product was reduced to the desired state of fineness by passing it through a sieve, and the sieved material was then dried. An additional step was introduced, in which the mashed potato was frozen prior to its admixture with seed powder. The resulting powder was more granular and less gelatinous than when this step was omitted.

Willets and Rendle (1948) found that, unless the moisture content of the mashed potatoes was reduced to about 40% before drying, the texture and palatability of the product would be unsatisfactory because of the rupture of potato cells and release of starch. They also found that, if the mashed potatoes were frozen and then allowed to thaw with subsequent centrifuging to remove up to 60% of the moisture, the product could be dried, without addition of any seed powder, to a satisfactory and readily reconstitutable mashed potato powder. However, even if the moisture remained as high as 60% and some seed powder was added to reduce it to 40%, there was still a considerable saving in the amount of seed powder needed, with a corresponding increase in output of the product.

Rivoche (1951) patented a process which consisted essentially of freezing cooked potato, then reducing the

particle size by rubbing, abrasive crushing or milling action to give a very fine frozen powder, and then subjecting it to a drying step. The intention was to separate and dry the cooked potato cells without damaging them excessively and obtaining an unsatisfactory product.

Greene et al (1948) developed a "freeze and squeeze" method in which mashed potatoes were frozen, thawed and pressed or centrifuged to reduce the moisture to about 60% before granulation and drying. The process toughened potato cell walls against mechanical damage. The product offered good texture on reconstitution, but lacked desirable taste and flavor.

A straight-through, or nonrecycling process for the production of potato granules was developed by Lazar et al (1964). Stepwise conversion of cooked potatoes into dry granules featured drying in stages as a new technique for separating the cells from one another. Few potato cells were ruptured during such drying and, therefore, not much starch was released. The product had a high bulk density and reconstituted readily.

An F-T process which omits precooking and cooling steps was recently disclosed by Ooraikul (1977). The process provided a new method wherein the overall effect was to cause very little damage to either the physical or nutritional properties of the product. In addition

there was very little discard or recycling.

An A-B process which is a modification of that of Rendle (1945) is the only technique used commercially at present. However, due to several disadvantages inherent in the A-B process, newly developed processes, such as the F-T process, which eliminate or minimize some of these problems, appear to have good commercial potential.

3.1.1 The Add-Back Process

The basic features of the process are: peeling, slicing, precooking or water blanching with subsequent water cooling; followed by steam cooking, mash-mixing (with about two parts or recycled dry granules), conditioning, remixing, air lift drying, fluid bed drying, cooling and sieving.

The rationale for the sequence of the steps is as follows: Slicing ensures effective and uniform heat transfer in subsequent cooking. Precooking and cooling avids sloughing during cooking and imparts the firmness to cell walls which is required in the mash-mixing step. Cooking brings about final softening of the tissue. Hot mash-mixing results in tissue separation into individual cells or aggregates, with minimum cell rupture. During this step there is addition of additives such as fatty acid monoglycerides, sulfite and antioxidants. Conditioning in a stream of cold air is needed to equilibrate

the mash moisture and, by keeping the moisture content above 30%, to force the free starch to retrograde and/or to form clathrates with glycerides, and thus increase the friability of the moist mash (Hadziyev and Steele, 1979).

Remixing is done in order to further granulate the moist mash into small aggregates or single cell particles. This and the previous mash-mixing step ensure that the moist granules remain separated when conveyed and dried in the subsequent air lift drying step. The latter step reduces the moisture content of the granules from 30% to about 15%, after which fluid bed drying decreases the moisture content to close to 7%.

The cooled granules are then sieved. A small portion (or particle size 80 mesh or less) is collected as end product, while the remainder is recycled. Particles of 10 mesh or greater are removed as rejects.

The A-B process has been improved, but its major disadvantage still remains: 1/10 to 1/6 of the solid material handled is the end product, while the remainder stays in the system by recycling. Granule quality may be reduced because undesirable characteristics, once developed, can remain in the system in appreciable amounts even after numerous cycles, perhaps for as long as a week of continuous production. This also tends to increase operating costs.

3.1.2 The Freeze-Thaw Process

The F-T process for the production of potato granules was developed to eliminate or minimize some of the major problems of the conventional A-B process (Ooraikul, 1978).

In the F-T process potatoes are peeled sliced, washed, and soaked in 0.5% $NaHSO_3$ solution for 5 minutes, after which they are steam-cooked for 35 minutes. The cooked potatoes, along with 0.25% Myvatex (w/w), are immediately mashed for 2 minutes in a mixer equipped with a flat beater. The mashed potatoes are then frozen in an air-blast freezer, and thawed at room temperature before being charged into the dryer bowl of a fluidized bed dryer, preheated to $70^{\circ}C$. In the predrying step the drying air is $93^{\circ}C$ at a velocity of 130 m/min, and the stirrer speed 20 r.p.m.. In the granulation step air temperature and velocity are reduced to about $30^{\circ}C$ and 15 m/min, respectively, while the stirrer speed is increased to 500 r.p.m.. Drying is done at $85^{\circ}C$ and 115 m/min air velocity. The dried product normally contains at least 85% of granules smaller than 60 mesh, and the broken cell count is not more than 3% (Figure 1).

The F-T process is simple to operate and control, and requires less intricate equipment to produce the same amount of product. The reconstituted mashed potato

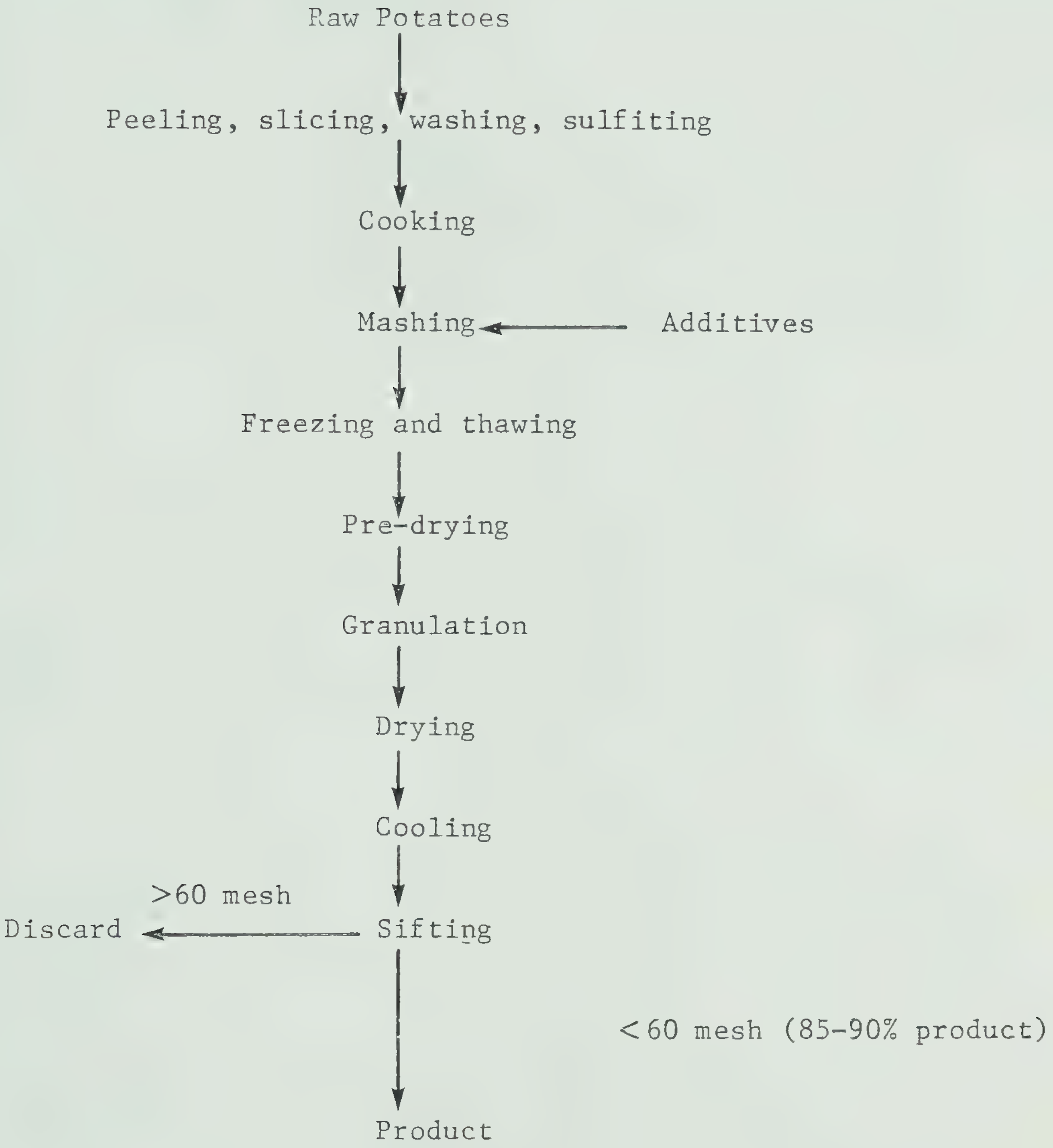

Figure 1 Flow chart of the freeze-thaw process.

from the F-T granules is superior in textural quality, and both the flavor and color of the product resemble those of freshly mashed potatoes (Ooraikul, 1974).

3.2 Storage Problems

As with most dehydrated products which contain sugar, protein and lipids, potato granules are subject to nonenzymic browning and oxidative deterioration during storage.

3.2.1 Nonenzymic Browning

Nonenzymic browning can occur during processing and storage of potato granules. It results in distinct deterioration in the color, flavor, and nutritional value of the product.

During processing, the browning reaction has a high temperature coefficient and the rate is exponential with temperature (Hendel et al., 1955). The use of potatoes with a low content of reducing sugars is one of the best measures to avoid browning during drying.

The extent of nonenzymic browning is usually proportional to the content of reducing sugars, although exceptions to this general rule do occur (Smith, 1977).

Potatoes with less than 1% of reducing sugars on a dry basis are best for the manufacture of granules. However, in order to hold fresh potatoes without undue

sprouting prior to processing, they must be stored at temperatures close to 5.5°C. The drawback is that at these temperatures there is a large increase in the reducing sugar content of the potatoes.

Conditioning treatment in which the fresh potatoes are held at about 21°C (70°F) for one or two weeks before processing can reduce the level of reducing sugars, but the treatment is only partially effective (Smith, 1977). In processing of potato granules it is a general practice to add sulfites to inhibit both nonenzymic and enzymic browning. Sodium sulfite and/or bisulfite are added along with emulsifiers, antioxidants and other additives in the mashing step of processing. The amounts used correspond to 350-500 ppm (as SO_2) in the dehydrated end product. The level of SO_2 in potato granules is subject to government regulation. In Canada, the United States, and the United Kingdom not more than 500 ppm are permitted (Hadziyev and Steele, 1979). Although lowering of moisture content of the product and avoiding of high temperatures during storage are effective in inhibiting browning in granules, they do not play any part in controlling the phenomenon during processing.

3.3 Lipids in Potatoes

Although the quantity of lipids in potatoes is

very low from the nutritional point of view, they do play a major role in oxidative deterioration of potato granules during storage. A detailed study of the lipid composition and constituents in raw and granulated potatoes was provided by Pun (1979). In that study it was found that lipids are only a trace constituent in potato tubers. Netted Gem potatoes contained 0.65% lipids on a dry weight basis.

The lipids found were compound, i.e., those containing other groups in addition to esters of fatty acids with glycerol. The major compound lipids were phospholipids, galactolipids and steryl lipids. The major phospholipids were phosphatidyl ethanolamine and phosphatidyl choline. The galactolipids found to be predominant were digalactosyl diglyceride and monogalactosyl diglyceride. The steryl lipids identified were free sterols, esterified sterols, steryl glucoside and esterified steryl glucoside. The so-called neutral lipid fraction was only a minor constituent of potato lipids, with triglycerides being its major component. The predominance of polar lipids (phospholipids and glycolipids) in the tuber was an indication that tuber lipids were primarily structural elements of cellular organelles and lipomembranes. They were all rich in polyunsaturated fatty acids. All lipid classes were esterified, mostly

by linoleic, linolenic and palmitic acids. Stearic and oleic acids were present to a lesser extent.

The most unsaturated potato lipids were the galactolipids, monogalactosyl diglyceride and digalactosyl diglyceride, which contained predominantly the unsaturated acids, linoleic and linolenic. On the other hand, the steryl lipids, esterified steryl glucoside and esterified sterol, being esterified mainly by palmitic acid, were among the most saturated potato lipids.

The sterol composition of the steryl lipids was also established. Only three sterols were found to be present in significant amounts: cholesterol, stigmasterol and β-sitosterol. The predominant sterol overall in steryl lipids was β-sitosterol, whereas cholesterol was concentrated in the esterified sterol and steryl glucoside fractions.

3.4 Lipids in Dehydrated Potatoes

A comprehensive study of potato lipids and changes in their constituents and fatty acid composition during production of granules by the F-T process was given by Pun (1979).

The relative amounts of individual lipids in raw potatoes did not change significantly during processing, however, their absolute amounts did decrease substantially.

The major loss occurred during the slicing/steam-cooking/ hot mashing steps. This loss was mainly in the phospholipid fractions. Phosphatidyl ethanolamine and phosphatidyl inositol were the most affected lipids. However, the loss of various lipids was not accompanied by an increase in the content of free fatty acids. On the contrary, the free fatty acid content decreased substantially. This finding would suggest that the lipids were lost in pre-cooking and cooling steps as a result of enzymic hydrolysis and degradation, followed by steam distillation of lipid breakdown products, since pure triglycerides and other lipids were not distillable under simulated conditions of cooking and/or mashing (Pun, 1979; Pun et al., 1980).

The relative fatty acid composition of total lipids changed slightly during processing. There was a slight accumulation in stearic and palmitic acids and a slight decrease in the amount of polyunsaturated fatty acids. Also, the fatty acid composition of the neutral lipids (triglycerides) did not change to any significant extent during processing into dehydrated granules. Hence, the unsaturation degree of all the lipids in freshly processed granules remained very high, so off-flavor development in dehyrated granules would not be surprising. In light of these results, galactolipids and phospholipids,

which contained the most unsaturated fatty acids, were likely to be major compounds associated with off-flavor development by autoxidation of potato lipids. However, the nature of lipids *per se* in potatoes appears to be of equal importance to the manner in which lipids are associated with cellular components and the changes in the spatial organization of these cellular constituents in potato tissue as induced by processing. The latter might be a factor in controlling the quality of potato granules, since during cooking and subsequent processing steps the lipids are embedded and/or spread over gelled starch, denaturated protein and/or cellulose-pectin matrices.

As found by transmission electron microscopy, lipids in cooked potato cells exist in the form of membranes sandwiched between gelled starch and the cell wall (Pun, 1979). Their oxidation would be partially prevented during granule processing, especially during drying steps, since they are not exposed directly to the drying air. However, this spatial arrangement of lipid constituents in dry granules would not be effectively shielded because both starch and cell wall in a dehydrated state would act not only as spreading matrices for the lipid but also as promoters of oxidative attack. Such a possibility would be greatly minimized if lipids in the processed product existed in combination with proteins, a combination which

retards lipid oxidation (Khan & Hadziyev, 1979).

In conclusion, the oxidation rates of phospho- and galactolipids in dehydrated granules would be a resultant not only of the structure and unsaturation degree of lipids but also of the nature of the matrix with which the lipids are associated.

3.5 Autoxidation

3.5.1 Possible mechanisms of Autoxidative Rancidity

Lipid autoxidation in potato tuber occurs when lipids react with atmospheric oxygen. Damage to the living tissue disrupts the internal biochemical control. Such disruptions can result from: a. physical damage (cutting or bruising of the tuber), b. infection by microorganisms, c. senescence or death of the tissue, and d. processing of tubers.

The mechanism of lipid autoxidation comprises three major steps (Labuza, et al., 1971):

1. The molecules of unsaturated fatty acids are excited in an initial step by energy of light or heat. This is a fast reaction which usually is not rate determining.
2. In the second step (propagation) there is a transfer of energy from one excited molecule to another; oxygen is tied up as a peroxide

free radical. This step has a rate constant (Kp).

3. In the final step (termination) peroxide free radicals are split by specific recurrent reactions, producing a wide variety of products which are offensive in taste and odor. In this step the initial product is usually an aldehyde resulting from direct scission of peroxide.

In practice it is important to realize that the presence of linoleic and linolenic acids or other polyunsaturated acids can lead to induced autoxidation of the more saturated fatty acids. Such an autocatalytic effect might involve a chain reaction with oleic acid, and a saturated fatty acid may even act as a substrate. In addition, autoxidation is strongly catalyzed by potato trace metal constituents (Cu, Fe). Thus, dehydrated products, like potato granules, are far more readily subject to oxidative rancidity than the corresponding raw potato tissue. The effect of trace metal catalysts is highly significant when dehydration is carried out beyond a certain moisture level. The only explanation for this is that the trace metals in such a product are free, and not complexed or coordinated with water molecules, or simply are more active in the nonpolar environment (Uri, 1973).

3.5.2 Autoxidation Problems in Dehydrated Potatoes

The high degree of unsaturation of potato lipids contributes to the gradual development of oxidative rancidity of dehydrated flakes and granules. The first extensive study of oxidative off-flavor development in granules was by Buttery et al (1961). In this study potato granules, prepared by the A-B process with sulfite (300 ppm SO_2) as the only additive, were packed in cans in an atmosphere of air, oxygen, or nitrogen and stored at room temperature. Control samples were kept under nitrogen at -35°C. The oxidative degradation of linoleic and linolenic acids closely correlated with the volume of oxygen absorbed and with the degree of off-flavor of the product upon reconstitution.

Since off-flavor development was due to the presence of polyunsaturated fatty acids, their content was expressed as an unsaturation ratio (UR, a ratio of the sum of linoleic and linolenic acids to the sum of palmitic and stearic acids present in the granules). The UR was suggested as a convenient index for the probability of autoxidation. Freshly dehydrated granules had a UR close to 30. This decreased to 12 after 4-5 months storage in air, and to 0.7 after 3 months storage in oxygen.

The oxidation rates of linoleic and linolenic acids were similar. It was established that two moles of oxygen

were taken up for each mole of linoleic and linolenic acids oxidized. Off-flavor scores for the stored granules, as obtained by a sensory panel, increased with a decrease in UR. Oxygen absorbed from the headspace plotted vs storage time gave a curve typical of lipid autoxidation. There was an induction period, followed by rapid oxidation (propagation step) and a tailing-off period.

Buttery et al (1961) also analyzed the headspace vapor of the can, and the vapor above hot reconstituted granules. They detected aldehydes (up to C_6) and hydrocarbons (up to C_5). Hexanal was the predominant volatile from granule autoxidation. Its concentration was about four times that of any other major component, and ten times that of the majority of the other compounds. The volatile from autoxidized granules corresponded to theoretically expected degradation products of linoleic and linolenic acids.

Evans et al (1969) postulated and proved thermal breakdown of hydroperoxides, yielding specific hydrocarbons. The oxidation of pure linoleic and linolenic acids produced mostly ethane and pentane, which together constituted more than 90% of the hydrocarbons released. Similar results were obtained for autoxidized potato granules.

Recently, measurement of the concentration of hydrocarbons (pentane in particular) was suggested for determination

of the extent of oxidative deterioration of dehydrated mashed potatoes (Arnaud & Wuhrman, 1974).

Potato granules stored in air do not show a high level of headspace volatiles, but there is a high concentration upon steam distillation, or in the headspace of hot reconstituted granules. This suggests that the bulk of off-flavor constituents derived from oxidized lipids are released through the breakdown of precursors after hot reconstitution of granules.

The relation of hexanal in headspace to subjective flavor estimates was reported by Boggs et al. (1964). Commercially produced granules (7% moisture, 2.5 ppm BHT, and 250 ppm sulfite as SO_2) were sealed in cans under air, and stored at 22°C. A control sample was packed under nitrogen and stored at -34°C. Air-packed granules, when reconstituted, showed a hexanal increase proportional to storage time. The increase was slow during the first two months, suggesting an induction period. This was followed by a rapid change after 80 days, after which a regular hexanal increase occurred up to 4 months of storage. Hexanal concentration was closely associated with flavor deterioration of dehydrated granules as judged by a test panel.

Walter and Purcell (1974) found that dehydrated sweet potato flakes underwent rapid oxidative deterioration

unless stored in an atmosphere low in oxygen. Of relevance to rancidity problems of dehydrated mashed potatoes was their suggestion that autoxidation of flakes occurred in a bimodal fashion, with free surface lipids being oxidized at a faster rate than internally located bound lipids. The loss of bound fatty acids was almost too slow to be detectable, while surface fatty acids had an induction period of 18 days. The fact that 76% of unsaturated lipids occurred in bound lipids and the bound lipids were oxidized at much lower rates than surface lipids strongly suggested that environment was often more important for autoxidation than lipid composition.

A plausible explanation of bimodal autoxidation in flakes was that processing brings about a trapping of up to 90% of the lipids within gelled carbohydrates and protein matrices. This matrix protection might retard lipid autoxidation. However, lipids on the flake surface are freely exposed to air and consequently, are readily oxidized. Therefore, the rancidity responsible for short shelf life of dehydrated mashed potatoes might be attributed primarily to surface lipids (Walter et al., 1972).

Khan and Hadziyev (1979), studying accelerated autoxidation of potato lipids in dehydrated model systems and potato granules, found that oxidation rates were highest with glycolipids, followed by phospholipids.

Neutral lipids, most of which were saturated, were oxidized very slowly. The authors suggested that in a processed potato product the most unsaturated lipids (galactolipids) would be most susceptible to degradation, and that this would be influenced by lipid orientation within or on the surface of the protein and/or carbohydrate matrices of the final product.

3.6 Packing and Storage

3.6.1 Atmospheric Storage

Volatile components associated with storage changes in dehydrated potato products can arise from reducing sugar-amino acid interaction and from lipid oxidation. Storage for six months, as reported by Sapers et al. (1972), resulted in only small increases in the content of low-boiling aldehydes, and of furfural. Phenylacetaldehyde, the major component of potato flake volatile concentrate, increased slowly during the first three months of storage, as did benzaldehyde. Differences between the level of furfural and the Strecker degradation aldehydes were small and variable in flakes packed in air and in nitrogen. These findings suggested that dehydrated potato granules and flakes packed in nitrogen might undergo further non-enzymic browning reactions during storage, yielding volatiles detrimental to flavor. However, the shelf life of flakes

was not normally limited by flavor defects due to sugar-amino acid interaction. The major objectionable flavor defect was derived from lipid oxidation, which could be controlled to a certain extent by BHA or BHT and by packing in nitrogen. Flakes stored in air at 23°C for up to 6 months showed a substantial increase in compounds clearly indicative of lipid oxidation.

The possible effectiveness of using cartons for storage of dehydrated mashed potatoes was tested by Lisberg and Chen (1973). Their study involved freshly processed granules (6% moisture, 11 ppm BHT, and 382 ppm sulfite as SO_2) stored at 24°C and 50% relative humidity under air or nitrogen in sealed cans or foil-lined and polyethylene-coated cartons. Hexanal was not detected until the third month of storage. Differences in flavor and aroma were significant only after the fourth and sixth months. The content of BHT declined steadily to 6.7 ppm in cans and 1.7 in cartons.

Overseas shipment of granules in polyethylene-lined paper bags during summer may result in extensive rancidity. Some shipments of add-back granules (7% moisture, 550 ppm sulfite as SO_2, and close to 10 ppm BHT) became rancid after a transportation period of four months (Dornay Foods, 1976).

Hexanal levels determined by the procedure described

by Buttery and Teranishi (1963) and Boggs et al. (1964) were 4 - 5 times higher than commercially permitted. The levels of SO_2 decreased at the same time and tended to reflect the extent of rancidity. The samples with minimal hexanal levels retained about 4 ppm of antioxidant, and the slightly rancid ones only traces, while the highly rancid granules completely lost all the antioxidant.

3.6.2 Nitrogen Storage

Oxidative deterioration can be retarded greatly by packing potato granules in nitrogen. However nitrogen has little effect on the rate of browning. Nitrogen packing is used commercially for control of oxidative deterioration. While oxidation is largely prevented, it still occurs to a much lower extent, presumably because of the small amount of residual oxygen that is usually present (the package usually contains 0.5-1.5% O_2). When pin holes occur in the foil laminate, heat-sealed bags usually used for retail distribution, oxidative deterioration may be severe. Packing in nitrogen, is, of course, of no further benefit after the container has been opened (Talburt and Smith, 1975).

It is evident from the foregoing discussion that lipids are primarily responsible for off-flavor in stored dehydrated potato products. Although packaging in an inert atmosphere is quite effective in preventing oxidative

deterioration, packaging and material costs are so high that other methods of preventing oxidative changes in potato granules are preferred. In commercial practice, incorporation of antioxidants into the dehydrated product remains the most practical and cheapest way of countering the oxidative deterioration problem.

3.7 Mechanism of Antioxidant Action

The majority of antioxidants which are used in foods are effective because they interrupt the chain propagation process of autoxidation (primary antioxidants). The formation of free radicals cannot be entirely suppressed, but can be retarded by a group of compounds able to complex heavy metal ions (secondary antioxidants). These compounds have little effect in the absence of primary antioxidants. However, they enhance or greatly prolong the action of primary antioxidants. Such synergistic ability has been ascribed to ascorbic and citric acids. However, in dry systems these acids function more as chelating agents which complex with trace metals, thus making them less available for the initiation step of lipid oxidation. In the presence of increased moisture, Ascorbic acid performs as a primary antioxidant (FAO Nutrition Meetings Report, Series #50 C, 1972).

Phenols are the most commonly used antioxidants

due to their light color, unobtrusive odor and taste, low toxicity and effectiveness at low concentrations. Widely used in dehydrated potatoes are BHA (a mixture of 2 and 3-tert-butyl-4-hydroxyanisole), BHT (di-tert-butyl-p-cresol) and PG (propyl gallate). However, the ability of BHA and BHT to remain active in food products after heat treatments like baking, frying or dehydration makes them the first choice as antioxidants (Lundberg, 1966).

Synergism in mixtures between BHA and BHT is usually additive. Synergism in mixtures between BHA and BHT as well as between BHA and PG provides increasing antioxidant potency. Therefore, BHA and BHT are usually added together in the mashing step of potato processing. In order to obtain a good distribution in the mash, they are added in an emulsion or in a solution using ethanol as a solvent. An example is a patent assigned to the American Potato Co. (1967) in which an ethanol solution of BHT is added to mashed potato prior to dehydration.

In freeze-dried whole foods where tissue integrity has been preserved, lipids are generally not well protected by synthetic antioxidants (Porter et al., 1977). However, these antioxidants do function well when they are incorporated and homogenized into the lipids in vegetable oils and lard. Hence, the poor protection in dried whole tissue foods, including granules or flakes, might be

due to the lack of ready access of the antioxidant to sites of oxidation, i.e., polyunsaturated polar lipids of the membrane systems of the tissue.

Antioxidant effectiveness in dried membranes on porous and dried model systems coated with a monolayer of linoleic acid was reported by Porter et al. (1977). BHA and BHT were 3.6- and 1.1-times , respectively, more effective than tocopherol, while caffeic acid was also superior (2.1-times). The caffeic acid result was of interest since it is one of the natural phenolic acids present in potato tuber. These model experiments showed that BHA was by far the most effective antioxidant on a silica matrix that simulated dry membranes. Model systems of microcrystalline cellulose, glycerol and methyl linoleate showed PG to be more effective than BHA, but only at water activities above those typical for dried foods (Labuza et al., 1971).

Improvements in shelf life with antioxidants in model systems consisting of methyl linoleate, glycerol and microcrystalline cellulose at water activities of 0.11 and 0.75 were reported by Ragnarsson et al (1977). It was found that the primary antioxidants, BHA and BHT, gave significant protection in a temperature range of 25-45°C when compared with PG and tocopherol. These authors also reviewed the value of procedures referred to

as accelerated shelf life tests (ASLT) in which the acceleration parameter is a substantial increase in temperature. They stressed the fact that predictions of room temperature shelf life based upon a single high temperature ASLT could not be done with any degree of confidence unless the reaction rate increase for a 10°C temperature rise (Q_{10}) was the same for the sample containing the antioxidant as for the control in which antioxidant is omitted. For a low water activity system (a_w 0.11) the normalized induction period (the time required for 3% of the linoleate to oxidize, divided by the time needed for a control) was 20 for BHA and 15 for BHT at 45°C. At room temperature the values were more than doubled. This illustrated that a single ASLT study at 45°C could lead to a significant underestimation of the shelf life extension at room temperature and, consequently, to a very significant overuse of antioxidant.

Activation energy (E_a) values were obtained for model systems used by Ragnarsson et al (1977). The E_a for a control of an a_w of 0.11 was 13 kcal/mole. In the presence of primary antioxidants it increased to about 20 kcal/mole. Ascorbic acid, instead of increasing the E_a of lipid oxidation, appeared to decrease it. Nevertheless, it was concluded that, in the presence of an effective primary antioxidant in the temperature range of 25-45°C, at least

part of the decreasing effect of the antioxidant on the oxidation rate occurred as a result of a rise in the E_a for lipid oxidation.

3.8 Use of Antioxidants in Dehydrated Mashed Potato

Relevant data about the effects of antioxidant treatment on flavor quality and stability of dehydrated mashed potatoes were reported by Sapers et al. (1975). Since efforts to stabilize the membrane lipids in a mashed potato system must content with the problem of dispersing fat soluble antioxidants in a medium containing close to 80% water, it was suggested that antioxidants in flake processing should be added as components of emulsions containing other ingredients, or as alcoholic sprays.

When levels of added BHA and BHT were 55-60 ppm on a dry weight basis, drying the mash on a single drum dryer reduced the levels to only 13-20 ppm, regardless of the method of antioxidant addition. This corresponded to a recovery of only 15-35%, which is still better than the 10% experienced in potato granule production in which a fluid bed dryer is used. The initial antioxidant losses resulted mostly from volatilization and steam distillation during the addition of antioxidants to the hot mash and during drying of the mash. However, additional losses of antioxidant were encountered during storage of flakes

for up to one year in air at 23°C. Under these conditions the losses of BHA were negligible, while those of BHT were 14-22%. Also, the method of antioxidant addition had only a small effect on the storage stability of air-packed flakes.

Mean flavor scores obtained by a taste panel complemented the results of gas chromatographic analysis of oxidation products in headspace and in volatiles isolated by steam distillation. These scores were the lowest in flakes to which BHA and BHT were applied by spraying and were the highest when BHA and BHT were added in an emulsion. After six months of storage, the oxidation product levels increased by the same amount regardless of method of addition, while after one year the levels were highest in the samples to which BHA and BHT were applied as an alcoholic spray and in those where they were applied in a corn oil solution using an aerosol sprayer. Neither the mean flavor scores nor the volatile oxidation product levels appeared to correlate with initial or final amounts of BHA and BHT. Indication that antioxidant concentration was inversely related to the level of oxidation products was observed only during the sixth to twelfth months of storage.

Sapers et al. (1975) also tested the stability of potato flakes containing quercetin or caffeic acid, or

their combination with BHA and BHT. The results indicated that all samples were initially satisfactory with respect to flavor scores and levels of volatile oxidation products. However, flakes containing just quercetin or caffeic acid alone deteriorated during storage twice as much as samples containing BHA and BHT. This poor performance of these natural antioxidants of the potato might be due to their low mobility in the dehydrated system or to the use of an inadequate concentration. However, higher concentrations probably could not be used in flakes because of their bitter flavor and the objectionable yellow color of quercetin.

A combination of quercetin with BHA and BHT applied as an ethanolic spray resulted in a flavor score, after six months storage, that was higher than flakes with BHA and BHT alone. Moreover, there were lower levels of volatile oxidation products after one year. Further research should be done in order to assess the potential value of such combinations.

The control of oxygen in headspace of cans appear to be a promising way to suppress rancidity. Deobald and McLemore (1964) found that type I antioxidants were effective with sweet potato flakes only when the oxygen level was 10%. Moreover, Drazga et al. (1964) found that exclusion of oxygen and its replacement with nitrogen provided

as good or better protection than addition of BHA, BHT or tocopherols to white potato flakes.

3.9 Methods for Antioxidant Analysis

An additional problem encountered during studies of the effectiveness of antioxidants is their quantitative analysis since their concentration in the product is normally at the ppm level. Several methods have been developed for processed foods, each with some inherent advantages and disadvantages. To further complicate the matter, the accuracy of the results appears to rely heavily on the extraction methods used to separate antioxidants from processed food matrices. Two general routes exist for the determination of antioxidants in foods. One is for foods with a high fat content such as nuts, processed meat foods, and some baked products and is of no relevance to this study, while the other is for low fat foods like some cereals, rice, and potato flakes and granules.

In dehydrated mashed potatoes the determination of phenolic antioxidants, though assumed to be standarized, is still subject to further improvement. Filipic and Ogg (1960) reconstituted dehydrated samples and recovered antioxidants by steam distillation. BHA was determined by reaction with Gibb's reagent, and the total antioxidant content by Emmerie-Engel's method (Emmerie and Engel, 1938).

The content of BHA was then calculated by difference. Colorimetric determinations, however, can be inaccurate if there is even a trace of sulfur dioxide in the dehydrated sample. In addition, color development is not specific for BHA and BHT. The presence of other reducing substances introduced for example, by the addition of spices, may give rise to overestimation of antioxidant levels. Color development is also sensitive to temperature and light, and consistent time control is usually necessary. More recent techniques are gas chromatography, spectrophotometry, fluorometry, and pulse polarography.

3.9.1 Gas-Liquid Chromatography

In recent years a variety of methods have been developed for the estimation of phenolic antioxidants by gas-liquid chromatography. In general they are more rapid than colorimetric detection methods and are much more sensitive. Many of the reported systems are suitable for BHA and BHT. Buttery and Stockey (1961) extracted BHA and BHT from potato granules with petroleum ether. The extract was concentrated and injected onto a column packed with diatomaceous earth (firebrick) coated with 20% Apiezon L. This method, although sensitive, requires aging of the column for 1 week at 220°C. Potato lipid, which is extracted along with the antioxidants, produces some base line noise, thus limiting the sensitivity at

which the detector can be used. However, the main error seems to result from incomplete extraction of antioxidants from the granules.

The method presented by Schwecke and Nelson (1964) uses a 10 foot aluminum column packed with SE-30 silicone gum (2%) and Tween-80 (1%) coated on chromosorb W-Type ABS, 70-80 mesh. In their procedure a 10 g sample of potato granules is extracted in a glass chromatography column with diethyl ether as eluent. Di-BHA (3-4 di-tert-butyl-4-hydroxyanisole) is added as an internal standard, and the eluate is concentrated and a μl aliquot injected for analysis at 150°C. The average recovery of antioxidants was 98.2%.

GLC procedures are accurate and reproducible, and in practice BHA and BHT can be detected at concentrations as low as 2 ppm. However, quantitative accuracy falls off rapidly below the 5 ppm level. The main problem in analysis by GLC seems to be contamination of the column by potato lipids. Hartmann and Rose (1970) suggested that a short precolumn of siliconized glass wool be located in the sample injection port block as a trap for nonvolatilized lipids. The trap must be frequently replaced.

3.9.2 Thin-Layer Chromatography Techniques

Spectrophotometric analysis of samples from

cereals after use of paper chromatography or thin-layer chromatography (TLC) for antioxidant purification might also be applied with dehydrated mashed potatoes, but the methods are time consuming and inaccurate at levels below 5 ppm. However, separation of BHA, BHT and PG using glass TLC plates with silica gel as absorbent and benzene as a solvent (Sahasrabudhe, 1964) did prove to be a rapid and reproducible method for quantitative separation of BHT and the 2- and 3-BHA isomers. If a similar method could be used with fused silica rods, wherein the developed rods are charred below a flame ionization detector and the amount of thermally generated ions is measured, the technique would be a simple, accurate and rapid method and the sensitivity level would be 0.01 ppm or better (Hadziyev and Beaulieu, 1980).

3.9.3 Spectrofluorometric Method

The overall simplicity of an analysis based on the intrinsic fluorescence of BHA is an attractive feature. Although the quantum yield for BHA is small, it is still adequate for a sensitive spectrofluorometric procedure. Dilli and Robards (1977) introduced the method for dairy products, oil and margarine, with a sensitivity for BHA of at least 0.01 ppm. BHT does not interfere since its quantum yield is very low. However, BHA must be isolated by short but vigorous steam distillation of

an acidified (0.2 M H_2SO_4) sample of 1-2 g. The excitation wavelength recommended for the distillate is 293 nm, while the BHA emission is ready at 323 nm.

3.9.4 Methods Based on Voltammetry

A voltammetric method was developed by McBride and Evans (1973) for the determination of sterically hindered phenolics, including antioxidants such as BHA, BHT, PG, tocopherol and tocopheryl acetate. They described a procedure for the rapid analysis of phenolic antioxidants in fat and tocopherols in foods from a single polarogram in a very short analysis time. An inexpensive voltammetric instrument was employed in their study with no novel features involved in the design. They used a voltammetric cell fitted with three electrodes. It was equivalent to a classical polarographic cell with one working electrode and an aqueous saturated calomel electrode (SCE) as the reference electrode. An additional platinum wire served as the third so-called counter electrode. The working electrode was a glassy solidified carbon paste electrode, which was sealed with epoxy cement at the end of a 5 mm glass tube. The surface of the glass tube-carbon rod assembly was polished with emery paper until it was quite smooth. Then, using a rotary polisher and alumina powder, the surface of the glassy carbon was brought to a mirror finish.

An organic solvent mixture of ethanol and benzene was used. Though numerous electrolytes ranging from potassium hydroxide to nitric acid were investigated, dilute sulfuric acid was found to be superior. Most analyses were performed using 0.12 M sulfuric acid in 2:1 ethanol-benzene (v/v). The reproducibility of the method was adequate. In a single voltammogram the peak potentials (in Volts) were: α-tocopherol, +0.57; β-γ-tocopherol, +0.67; δ-tocopherol, +0.74; BHT, +1.03; and BHA, +0.78. The peak potential of BHA practically coincided with that of δ-tocopherol, hence, BHA can only be determined if the sample does not contain appreciable amounts of this tocopherol isomer.

The advantage of the method is the rapidity of analysis compared to a conventional GLC procedure. A small disadvantage is that the electrode surface must be polished in order to ensure reproducibility and high sensitivity.

Waltking et al. (1977) compared the voltammetric method to a GLC procedure for determination of tocopherols in vegetable oils. Voltammetry was found to be much more rapid and 2-3 times more precise. Attempts to establish the validity of the slightly higher apparent values for α- and γ-tocopherols obtained by voltammetry implicated gas chromatography *per se* or tocopherol derivative formation

as the source of error, rather than the extensive prior manipulation of the sample for chromatography. Essentially, fairly consistent results were obtained for α-tocopherol regardless of the technique used. However, more variable results, which were product dependent, were obtained for γ- and δ-tocopherols when the GLC method was applied.

In an attempt to improve the sensitivity of the voltammetric method, differential pulse voltammetry was applied by Podlaha et al. (1977) to simultaneously record the presence of α-, γ- and δ-tocopherols. The results by pulse voltammetry and high performance liquid chromatography were compared. An analysis by t-test at the 99% significant level showed no differences for the determinations of α-tocopherol, but some differences were found for the other isomers. The voltammetric method was found to be uncomplicated and, therefore, suitable for routine work. The differential pulse technique, as compared to a nonpulse, voltage ramp mode, is more sensitive and offer increased resolution between neighboring peaks.

Differential pulse voltammetry was applied successfully by Haydar and Hadziyev (1979) in the analysis of tocopherol, carotene, BHA and BHT present as additives in dehydrated potato granules. Generally, potatoes do not contribute a significant amount of tocopherols to the

diet. Bunell et al. (1965) reported the mg % of α-tocopherol and total tocopherol to be, respectively, 0.053 and 0.085 for raw, 0.027 and 0.055 for baked, and 0.043 and 0.061 for boiled potato. Tocopherol was not detected in granules of the potato cv. Netted Gem. Since α-carotene had a half-wave potential of +0.58 V, it did not overlap with the half-wave potentials of BHA and BHT, while β-carotene did not interfere as it is present only in the yellow potato cultivars. BHA and BHT were accurately determined since their half-wave potentials were well separated: BHA, +0.78 V and BHT, +1.03 V.

Based on the above, differential pulse voltammetry was chosen as the method in this study for simultaneous determination of BHA and BHT in dehydrated potato granules.

4. PREPARATION OF POTATO GRANULES
WITH THE F-T PROCESS

4.1 Materials

Southern Alberta grown Netted Gem potatoes of Specific gravity 1.097 (25± 1% dry matter content) were obtained from "Iwabuchi and Sons Ltd.", Edmonton.

Sodium bisulfite ($NaHSO_3$) was from J. T. Baker Chemical Co., Phillipsburg, N.J.

Myvatex (a blend of 58% propylene glycol monoester with 42% distilled monoglycerides, prepared from hydrogenated soybean oil, with not more than 0.02% citric acid added) was supplied by Kodak DPI, Rochester, N.Y.

4.2 Equipment

Abrasive potato peeler, Model 6115, The Hobart Mfg Co., Don Mills, Ontario.

Commercial Mixer, Model D-330-T, equipped with a wire beater, The Hobart Mfg Co.

Vegetable Slicer, Model H 4212, The Hobart Mfg Co.

Atmospheric Steam Cooker with cover lid.

Stainless steel baskets, 22 x 20 cm x 10 cm height.

Stainless steel trays, 60 x 46 cm.

Air blast freezer with minimum air temperature of

$-29^{\circ}C$ and air velocity of 1.42 $m^3\ s^{-1}$.

Manesty Petrie Fluid bed dryer, Model MP 10E as modified by Ooraikul (1973). Manesty Machines Ltd., Speke, Liverpool, England.

Speedomax 12 point temperature recorder. Leeds and Northrup Canada Ltd., Ontario.

Canadian Standard sieve series, and portable sieve shaker, # PX-21, The W. S. Tyler Co. Canada Ltd., St. Catherines, Ontario.

4.3 Procedure

The raw potatoes were peeled, sliced, washed and soaked in 0.1% $NaHSO_3$ solution. A batch of 1.5 kg was loaded into each of the stainless steel baskets and steam-cooked for 35 minutes under atmospheric pressure. The cooked potatoes, along with 0.25% of surfactant (Myvatex), as recommended by Ooraikul and Hadziyev (1974), were immediately mashed for 2 min in the Hobart mixer equipped with a wire beater. The speed of the mixer was approximately 400 rpm. Whenever required by the experiment, antioxidants were incorporated at mashing time.

The mashed potatoes (3 kg) were spread about 1 cm thick on a stainless steel tray and frozen over night in the air blast freezer at $-28^{\circ}C$ to $-29^{\circ}C$. The frozen potatoes were thawed to about $0^{\circ}C$ at room temperature before

being charged into the fluidizing bowl. The bowl was fitted with a blade stirrer and a collection bag. Temperatures of drying air and exhaust air were recorded on the Speedomax recorder, and the air velocity through the fluidized bed was regulated by a regulating valve in the exhaust pipe.

Predrying was performed with incoming air temperature of 85°C and velocity of 130 m/min, and stirrer speed of 30 rpm. It took 20-30 min to reduce the moisture of the mash to the desirable 40-45% level. At this stage the product was in the form of small aggregates of a few cells which were carried in the air stream to the cyclone collector.

The predried product was recharged into the drying bowl after the blade stirrer was replaced with the beater stirrer. Granulation was then performed at 25-30°C, with an air velocity of 30-50 m/min and stirrer speed of 400 rpm. Granulation took 8-10 min during which cell aggregates were separated into fine granules of single or a few cell units which were carried in the air stream to the cyclone collecting bowl.

The fine granules were recharged into the fluidizing bowl for final drying at 85°C with a 115 m/min air velocity and no stirring. Drying took 10-15 min, after which the dried granules were sifted through a series of

10, 18, 30, 35 and 60 mesh sieves on the sieve shaker. The particles which passed through the 60 mesh sieve were packaged as product and used for further experiments. Every batch followed the same processing procedure except for the experiment on the effect of changes in processing temperatures on antioxidant retention, where the predrying and drying air temperatures were lowered to 50 and 60°C, respectively.

5. APPLICATION OF ANTIOXIDANTS

5.1 Materials

BHT, crystalline (2, 6-di-tert-butyl-p-cresol), analytical grade, Sigma Chem Co., St. Louis, MO.

BHA, anhydrous (mixed isomers 2: and 3-tert-butyl-4-hydroxy anisole), Sigma Chemical Co., St. Louis, MO.

Ethanol, anhydrous, Baker analyzed reagent, J. T. Baker Chem. Co., Phillipsburg, N.J.

Tween 60 (Polysorbate 60), Atlas Chemical Industries, Brantford, Ontario.

5.2 Equipment

Kitchen Mixer, Type KM32, Braun AG, Frankfurt.

Turbula Mixer, Type T 26, Willy A. Bachoefen, Basil, Switzerland.

Virtis "45" homogenizer, Type Super 30, Virtis Research Equipment, Gardiner, N.J.

Atomizer (connected to a compressed air line), 100 ml capacity, Desaga, Heidelberg, West Germany.

Mortar and pestle

Burette (50 ml).

5.3 Methods

Antioxidants were applied to cooked and mashed potatoes in three major forms:

5.3.1 Powder

BHT and BHA or BHA alone were finely ground in a mortar before use. For complete and uniform incorporation, the powder was added only during mashing of potatoes with the temperature of the mash at least 70°C.

5.3.2 Emulsion

Two formulations of emulsion were tried.

Emulsion #1 consisted of:

Myvatex	0.25% w/w (based on cooked potato weight of approx. 80% moisture).
Antioxidants	as required by the experiment.
Water	2.25% v/w (based on cooked potato weight).

Antioxidants and Myvatex were mixed and ground in a mortar. The mixture was then added to water preheated to 80°C, and homogenized with the Virtis "45" homogenizer until a soft, milky emulsion formed.

Emulsion #2 consisted of:

Myvatex	0.15% w/w (based on cooked potato weight).

Tween 60	0.10% w/w (based on cooked potato weight).
Antioxidants	as required by the experiment.
Water	2.25% v/w (based on cooked potato weight).

Antioxidants and Myvatex were dispersed in Tween 60, then added into water preheated to 80°C, and homogenized with the Virtis "45" homogenizer at slow speed to obtain a soft, milky emulsion. The emulsion was incorporated into the product by dripping it from a burette onto hot potatoes while they were being mashed.

5.3.3 Ethanol Solution

The required amount of antioxidants was dissolved in a small volume of absolute ethanol (approx. 100 ml of ethanol solution were prepared for 4 kg potatoes) before being applied to the product. The solution was incorporated into the product by either spraying it with an atomizer or dripping it from a burette onto the product during mashing or mixing. The ethanol solution could be easily incorporated into the product at any stage of processing since the solution does not contain surfactants which require addition exclusively during mashing. Therefore, the effect of processing on antioxidant retention was determined by adding it to the product at various stage of processing.

This included:

a) Application at the mashing step by spraying and/or dripping.

b) Application at the thawing step by spraying the solution onto the mashed potatoes before predrying.

c) Application of half of the quantity at the mashing step and the remainder at the thawing step.

d) Application to dehydrated potato granules by spraying and mixing in a Turbula mixer, and by dripping and mixing with a wire beater in a Braun Kitchen mixer.

5.4 Moisture Content

Mositure content on potato samples was determined from the average weight loss from 3 replicates after heating 10 g of each at 55°C for 5 hr then at 105°C for 2 hr in a mechanical convection oven.

6. ANALYSIS OF BHA/BHT IN DEHYDRATED POTATO GRANULES

6.1 Materials

6.1.1 Reagents

Benzene. Analar BDH Chemicals, Toronto, Ontario.

Ethanol, anhydrous. Baker analyzed reagent, J. T. Baker Chemical Co. Phillipsburg, N.J.

Sulphuric acid. A. C. S. Reagent, Fisher Scientific Co., Fair Lawn, N.J.

6.1.2 Equipment

Chromatographic Columns, 25 x 1 cm i.d. with porosite fritted disc (ASTM 25-50 μm) and removable Teflon stopcock.

Volumetric flasks, 10, 50, 100 and 200 ml.

Steam Distillation Unit

1. Electrothermal mantle, 2L
2. Round bottom flask, 24/40 joint, 2L
3. Three-way Claisen distilling head, 24/40 joint
4. Thermometer, $-10^{\circ}C$ to $+360^{\circ}C$, 10/30 joint
5. Distillation tube adapter, 24/40 joint
6. Three neck flask, 24/40 vertical joints, 1L
7. Tube adapter, 24/40 joint

8. Condenser, West type, 500 mm, 24/40 joints
9. Condenser adapter, 24/40 joint

Distillation Unit

1. Glas-col heating mantle, 100 ml. Glas-Col Apparatus Co., Terre Haute, In.
2. Round bottom flask, 100 ml, 24/40 joint
3. Two way connecting tube, 24/40 joints, with 10/30 joint for thermometer
4. Thermometer, -10°C to +360°C, 10/30 joint
5. Condenser, West type, 300 mm, 24/40 joints
6. Condenser adapter, 24/40 joint

Instruments

Houston Omnigraphic X-Y Recorder, Model 2200-3-3

Polarographic Analyzer, Model 174A

Saturated Calomel Electrode, #9311; glassy Carbon Electrode, #9333; and Polishing Kit, #9320, all by Princeton Applied Research Co., Princeton, N.J.

Pyrex glass cell with Pt wire counter electrode

6.2 Procedure

6.2.1 Extraction of BHA and BHT

Differential pulse voltammetry analysis of phenolic antioxidants is not directly applicable to dehydrated potato granules since the antioxidants are dispersed and

trapped in potato matrices. Therefore, it is necessary to isolate and often to concentrate the antioxidants present in the sample.

Extraction of antioxidants from dehydrated potato granules was performed by the method suggested by Haydar and Hadziyev (1979). A glass chromatographic column was filled with a 5 g sample of dehydrated granules. The antioxidant was eluted with benzene, collecting 10 ml of effluent. In preliminary assays the recovery within the first 5 ml effluent was 96.8% of the total amount of BHA added into the granules. Additional volumes of effluent did not contain detectable quantity of the antioxidant. Similarly, a recovery of 95.3% for the first 5 ml extract was obtained for BHT (Figure 2).

The same method was used for extracting the antioxidants from samples taken during different stages of processing, as long as the moisture content of the sample was not higher than 40%. Samples with higher moistures yielded a water-benzene extract unsuitable for differential pulse voltammetry analysis. Bieth et al. (1978), in their comparative study of the principal methods of separation, established that only two methods can give good results with high moisture samples, i.e., continuous extraction with ethanol, and steam distillation as described by Filipic and Ogg (1960). The steam distillation

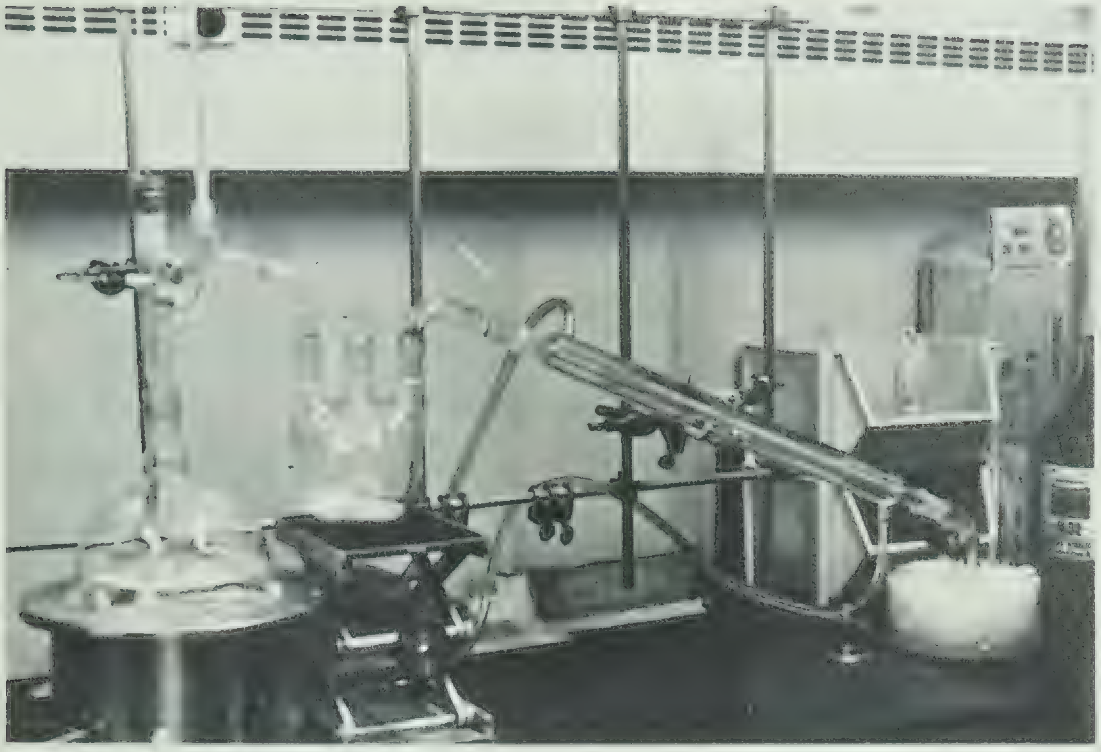

Fig 3 Steam Distillation Unit

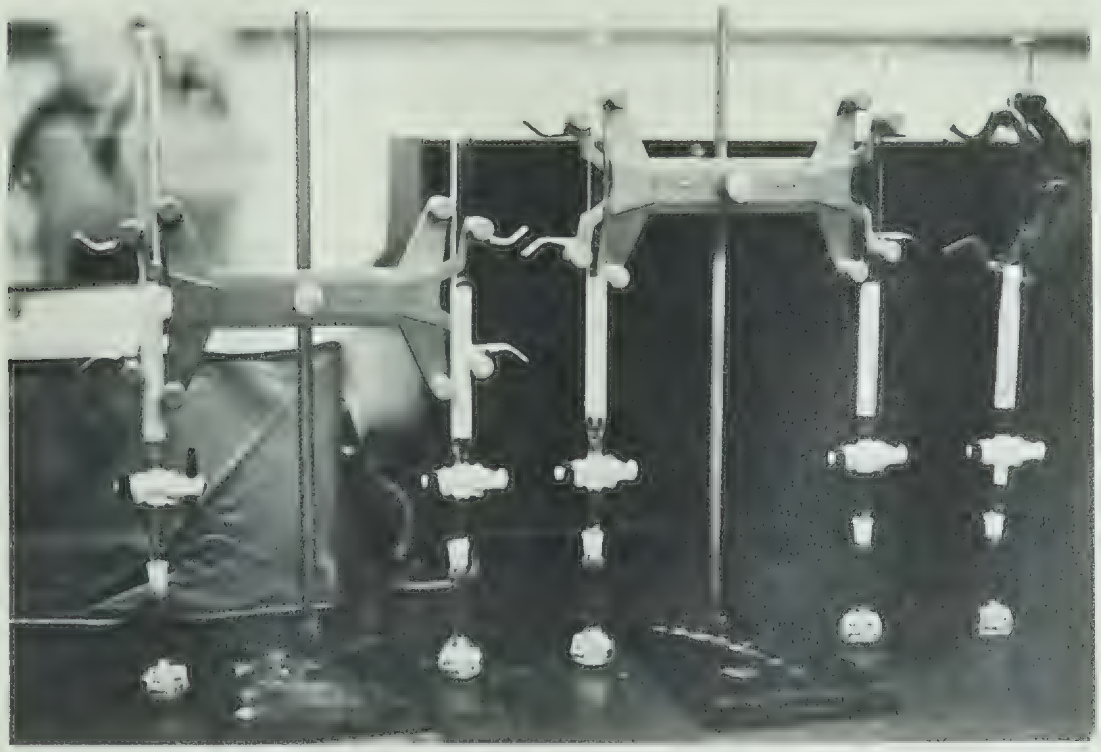

Fig 2 Chromatographic Columns Unit

method was used in this study to separate antioxidants from potato samples containing more than 40% moisture.

6.2.1.1 Steam distillation

Deionized water (1.5 L) was added to the steam generator. A 50 g sample of potato granules was introduced into the still and mixed well with 200 ml of water. A graduated flask was placed under the condenser tip, and immersed into a crushed ice bath. The heating rate for the steam generator was controlled so that vapor entering the condenser exitted completely condensed. The content of the sample flask was boiled gently to allow the generated steam to flow through the sample without condensing. The steam flow was adjusted to give about 20 ml condensate per minute. After approximately 260 ml were collected, the steam was turned off and the condenser rinsed with distilled water (Figure 3).

A preliminary recovery assay was made using 50 g of mashed potatoes containing a known amount of antioxidant and collecting five volumes of distillate. The assay showed that the first fraction collected (200 ml) contained 74.6% of the amount of antioxidant added, the second fraction (30 ml) 17.0% and the third (30 ml) 8.5%, while additional fractions did not contain detectable amounts of antioxidant. Hence, it was concluded that a distillate of about 260 ml would give adequate antioxidant recovery

under the standarized method of distillation.

The distillate was transferred to a separatory funnel and the antioxidant was extracted five times, each time with 10 ml of benzene. The combined extracts were concentrated to 5 ml in a semimicro, all-glass distillation assembly. The concentrate was transferred quantitatively to a 10 ml volumetric flask. The distillation flask was rinsed with benzene and the volume of the concentrate was made up to 10 ml.

The procedure described above essentially followed the steam distillation procedure given by Filipic and Ogg (1960), except that the trap containing MgO suspension as used by Filipic and Ogg (1960) was needed to remove phenolic and acidic components in the distillate that interfere with the color reactions for both BHA and BHT in the standard colorimetric determination. Since such interference does not occur in pulse voltammetry, the trap was omitted. In addition, Sloman et al. (1962) reported that as much as 1 ppm of BHT from a sample containing 5 ppm is absorbed by the MgO suspension. The amount trapped remains about the same regardless of the amount of BHT in the sample. Hence, proportionally larger amounts of BHT are lost as the amount of BHT to be determined becomes less. They also reported that heating the trap could prevent this loss. All these facts illustrate the advantages

of the methods used in this study.

6.2.2 Voltammetry Assay

Concentration Range in the Extracts:

-BHA, 1-30 ppm; BHT, 4-30 ppm.

Supporting Electrolyte:

-0.12 M Sulfuric acid in, ethanol-benzene 2:1, v/v.

Anodic Half-wave Potentials of the Peaks

-BHA, 0.67 V; BHT, 0.93 V.

An aliquot of 5 ml of the benzene extract was diluted with 10 ml of ethanol to reach the solvent ratio of 2:1 ethanol-benzene, and 1.5 ml of the electrolyte (0.12 M sulfuric acid in ethanol-benzene, 2:1, v/v) was added to make a total volume of 16.5 ml. A volume of not less than 15 ml was necessary to cover the level of the platinum counter electrode in the voltammetric cell. The solution was then analyzed in the differential pulse mode. All experiments were performed at room temperature (approx. 21^{O}C). Quantitation was made from the peak heights via a calibration curve (Figure 7).

In order to obtain reproducible results, a standard pretreatment procedure was applied before running the voltammogram. The carbon electrode surface was polished on a fine cloth tissue with alumina powder in order to remove the absorbed compounds which could interfere during

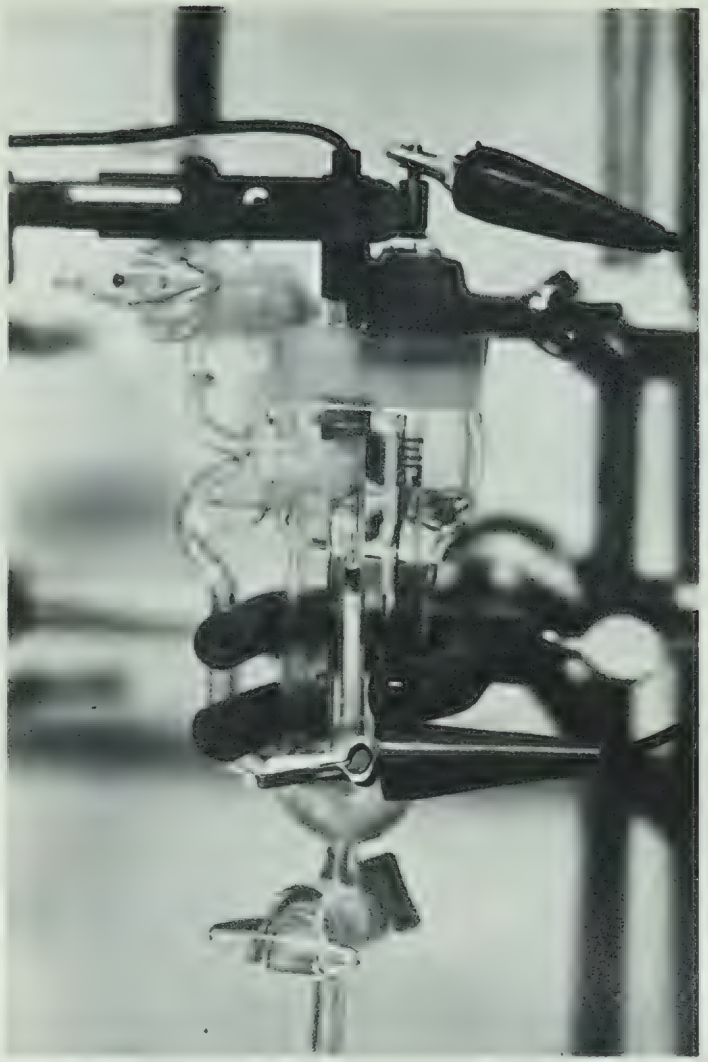

Fig 4 Pyrex glass cell with Platinum wire Counter Electrode, Saturated Calomel Electrode and Glassy Carbon Electrode.

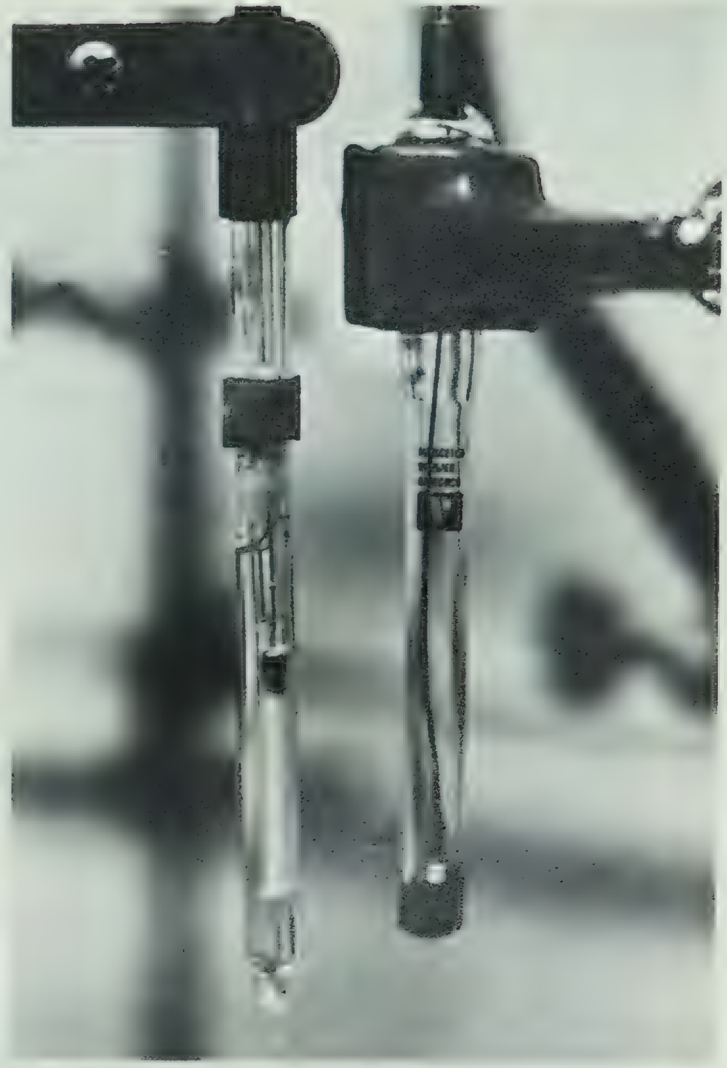

Fig 5 Saturated Calomel Electrode (left) and Glassy Carbon Electrode (right)

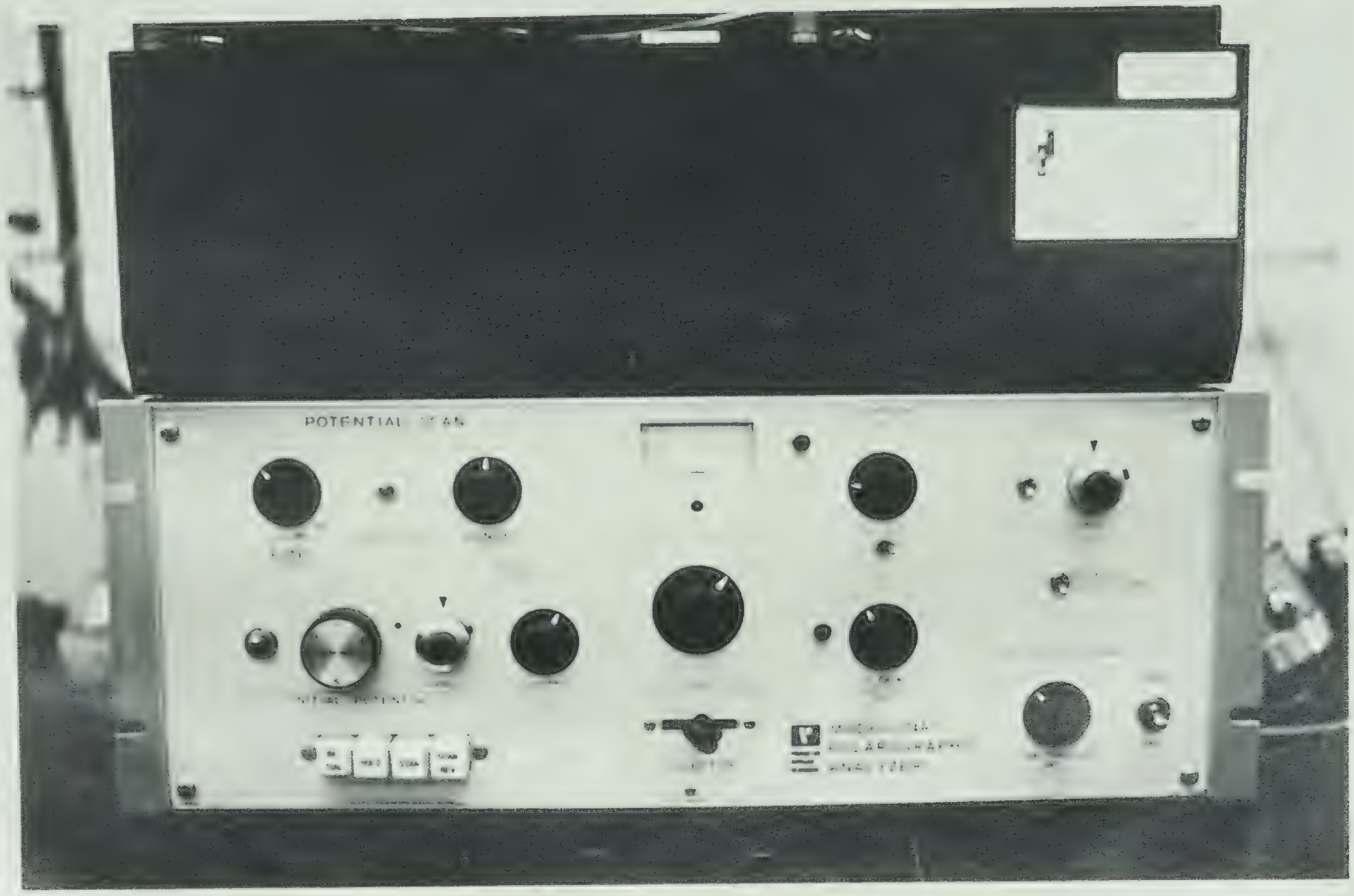

Fig 6 POLAROGRAPHIC ANALYZER

analysis. All other electrodes were wiped clean between sample analyses with a Kleenex tissue moistened with ethanol-benzene, 2:1, v/v.

6.2.2.1 Instrument Settings

Mode:	Differential Pulse
Supporting electrolyte:	0.12 M sulfuric acid in ethanol-benzene, 2:1, v/v
Electrode:	Glassy carbon
Initial potential:	+0.3 V
Scanning rate:	2 mV/sec
Scanning direction:	+ (positive)
Scanning range:	+0.3 V to +1.5 V
Pulse amplitude:	50 mV
Current range:	50 μA
Output offset:	off
Drop time:	0.5 sec
Display direction:	- (negative)
Low pass filter:	off
Output-offset	adjusted to desirable starting point

6.2.2.2 Calculation of Concentration: μg antioxidant/g sample (ppm)

Peak height = x = μg/ml (ppm/ml)

Sample dilution:

5 ml benzene extract

10 ml ethanol

1.5 ml sulfuric acid, 0.12 M, in ethanol-benezene 2:1 v/v

Total 16.5 ml

x (µg/ml) x 16.5 = amount of antioxidant in original 5 ml benzene extract.

The value is multiplied by 2 to obtain the quantity of the antioxidant in the original 10 ml extract from 5 g dehydrated potato granules.

$$\frac{\text{Peak height } (\mu g/ml) \times 16.5 \times 2}{\text{Weight Sample (g) dry (or wet) basis}} = \mu g/g \text{ (ppm dry or wet basis)}$$

7. STORAGE OF DEHYDRATED POTATO GRANULES

7.1 Materials

1. Bags

   Polyethylene bags (3 mil), 20 x 16 cm.

2. Equipment

   Controlled temperature oven. Thelco Model 6, Precision Scientific Co., Chicago, IL.

   Temperature Controlled Chamber, Labline Inc., Chicago, IL.

7.2 Methods

Samples of 50 g dehydrated potato granules were heat-sealed in polyethylene bags and stored for a period of 6 weeks at 37°C in a controlled temperature oven and at 25°C in a controlled temperature chamber. Samples were taken after the third and sixth weeks of storage for voltammetric determination of retained antioxidants (BHA and/or BHT) and moisture content determination.

8. RESULTS AND DISCUSSION

8.1 Analytical Techniques

The reliability of the voltammetric method for the determination of antioxidants applied by McBride and Evans (1973), as improved by Haydar and Hadziyev (1979) by the utilization of the differential pulse mode, was confirmed for dehydrated mashed potatoes. The tocopherols and α-carotene extracted from the granules were undetectable under experimental conditions. Calibration curves in a concentration range of 4 to 40 ppm for BHA and BHT showed an excellent linearity of the current output signal peak height vs concentration plot (Fig. 7). Correlation coefficients between peak height and concentration were very high, with values of 0.98-0.99 (significant at $p = 0.01$). Samples were diluted when necessary to permit analysis in the linear region of the plot.

Although the electrode pretreatment procedure was always applied before a sample run, it was found that the glassy carbon electrode loses its sensitivity after extensive use, causing a decrease in the slope of the calibration curve. Therefore, the sensitivity of the electrode was checked regularly with a set of standard antioxidant solutions. If there was a change in peak

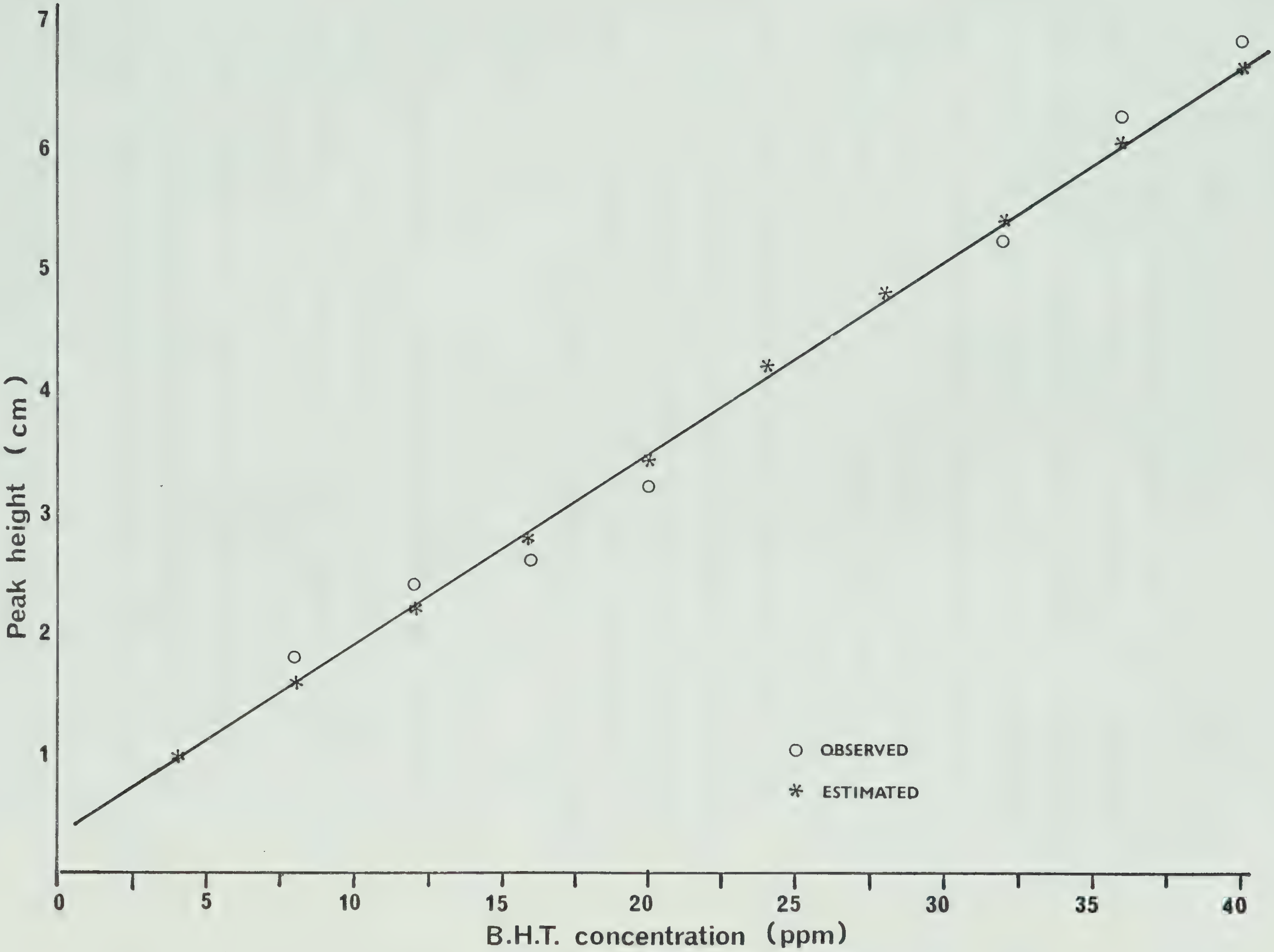

Figure 7 BHT Standard curve. Peak height (cm) vs concentration (ppm)

heights from the previous calibration curve, a new calibration curve was prepared and applied. To determine the possible interference by tocopherols and α-carotene, a blank sample (dehydrated potato granules without antioxidants) was extracted with benzene and a voltammogram was run on such an extract. No detectable peaks were found for tocopherols or α-carotene, and the voltammetric curve was similar to that given by a solvent-electrolyte blank. The entire analysis took only a short time, and the accuracy and reproducibility of the results were good. This technique was also favored by the fact that no prior treatment or separation procedures were necessary for dehydrated potato granules. Consequently, the analytical procedures are suitable in this application.

During the experiments involving samples from different stages of granule processing, it was found that the degree of hydration has a great influence on the extent of benzene extraction. Extractions from partially hydrated samples, with moisture contents of 30% or less, were reliable, but higher degrees of moisture reduced the extractive capacity of benzene and produced a cloudy extract because of emulsification of water in benzene.

As stated earlier, only two methods give good

results for extraction of antioxidants from dehydrated mashed potatoes, continuous extraction with ethanol and steam distillation. Since ethanol becomes diluted with water from the sample, it loses its extractive ability and miscibility capacity with benzene, hence, this technique was not acceptable. On the other hand, steam distillation gave good results for the mash and predrying samples (more than 30% moisture), with 97.3% recovery of antioxidants.

At least duplicates of samples were taken for antioxidant analysis. The variation between replicates tended to be greater in samples when antioxidants were applied in an ethanol spray than in samples when antioxidants were applied in an emulsion or directly as a powder. This may be because part of the antioxidant in the ethanol spray was lost through evaporation of some of the volatile fine mist. Also, once the ethanol spray did come in contact with the hot mash, the antioxidant would be rapidly absorbed into potato cells near or on the surface of the mash and could not be easily dispersed, resulting in nonuniform distribution of the antioxidant. When applied as a power or emulsion, on the other hand, the antioxidant would be dispersed fairly well by mashing action before any absorption could occur.

8.2 Application of Antioxidants

Dehydrated potato, with a fat content less than

1%, is a typical example of a low fat food product. Phenolic antioxidants (BHA, BHT and PG) have been widely used in dehydrated potatoes to prevent or minimize autoxidation. Crystalline BHA or BHT, or their solutions are quite often used for this application. The volatility of these antioxidants appears to be beneficial characteristic when they are used in the processing of potato granules.

It has been found that small quantities of BHA or BHT added to potato mash prior to drying steps will disperse by volatilization or steam distillation, resulting in protection of the product during processing and subsequent storage.

The small quantity of antioxidant which finds its way into the lipid portion of the product under these conditions is apparently adequate to provide a high degree of protection. However, because of the volatility of some antioxidants, particularly those with phenolic structures, their loss through steam distillation during processing of high moisture foods can be substantial (Sherwin, 1972), even under less strenuous processing conditions such as in freeze-drying (Kirleis and Stine, 1978). The loss may, to a certain extent, be reduced through the use of suitable application techniques.

In the production of potato granules with the

F-T process, application of BHT or BHA in powder form during mashing may be the most appropriate method, as the antioxidant and surfactant should be relatively well dispersed in the mash due to the high temperature (70°C) and the mashing action. Uniformly distributed antioxidant would protect the reorganized and newly exposed lipid membranes within the cells against oxidation during mashing and subsequent steps of the process where relatively high temperatures are applied. However, the results in Table 1 show that the loss of the antioxidant was the highest during the early stages of the process when only about half of the moisture was evaporated. Approximately half the content of BHT and BHA was lost during mashing and predrying steps. A further 20% of BHT was lost during granulation, which took place at about 30°C, and an additional loss of 15% occurred during drying, when the temperature was raised to about 85°C. BHA appeared to follow a similar pattern of loss during the process, though its second major loss (35%) took place during drying. In the final product 15% of BHT was retained as compared to only 5% of BHA. This appears to indicate that BHT has a greater "carry through" capacity than BHA with respect to the F-T processing conditions.

The results are in sharp contrast with those of Kirleis and Stine (1978) who found that BHA was retained

better than BHT in their model freeze-dried system. The difference may be attributed to the fact that the F-T process is operated under atmospheric pressure and a drying air temperature of up to 85°C, while the freeze-dry system is operated under high vacuum and the product remains frozen throughout the drying cycle.

It was noted in the current study that samples taken for the analysis of antioxidants varied widely in their antioxidant content. In some cases one sample contained 5-6 times greater antioxidant content than the others. This indicated that the antioxidant was not uniformly dispersed throughout the product during mashing. The antioxidant was not well distributed until after predrying, when the variation between samples was much smaller (Table 1).

The difficulty of dispersion and bringing the antioxidant into effective contact with lipid sites in a potato cell was partially overcome in a potato flake process by applying antioxidant in an emulsion or an ethanol solution spray.

In the present study two emulsion formulations were tried with the F-T process. Emulsion #1 consisted of BHT, Myvatex and water, and Emulsion #2 consisted of BHT, Myvatex, Tween 60 and water. Both were homogenized into a milky consistency and each was applied from a

Table 1. Retention of BHT and BHA through various steps of the F-T process when applied during mashing in powder form together with the surfactant Myvatex

Processing step	% Moisture	BHT Retention		% Moisture	BHA Retention	
		p.p.m.	%		p.p.m.	%
Before mashing	76.0	2,083	100.00	76.7	2,146	100.00
After predrying	31.7	1,078±362	51.75	39.9	1,032±131	48.10
After granulation	17.5	664± 17	31.88	27.3	887± 41	41.33
After drying	8.4	306± 17	14.69	13.1	107± 2	4.99

Antioxidant concentration was calculated on a dry matter basis.

burette dropwise into potatoes during the mashing step. However, as shown in Table 2, almost 97% of the antioxidant was lost during mashing and predrying for both types of emulsion. In the final product only 1% of BHT was retained when Emulsion #1 was used, and all was lost when Emulsion #2 was applied. Thus, Emulsion #1 seemed to offer slightly better retention than emulsion #2, and, since it was easier to prepare, it was exclusively used in further experiments with emulsions. When BHA replaced BHT in emulsion #1, the retention was slightly improved by 2.57%. These results indicated that the volatility of the antioxidants was increased substantially when in an emulsion, allowing greater loss through steam distillation during the process.

It was thought that retention of the antioxidants might be improved by lowering the predrying and drying temperature of the F-T process. However, this was not the case, as shown in Table 3 where there was no retention when the temperature of the two steps was lowered from 85 to 60°C, and only about 2% was retained when the temperature was 50°C. This was apparently due to the fact that at a lower temperature it took a proportionately longer time to lower the moisture content of the product to the desired level in each of the processing steps, thus resulting in an even greater loss of

Table 2. Retention of BHT and BHA through various steps of the F-T process when applied in an emulsion during mashing. Two formulations of emulsion were applied: #1. A mixture of Myvatex, BHT or BHA and water; #2. A mixture of Myvatex, Tween 60, BHT and water.

	BHT emulsion #1			BHT emulsion #2			BHA emulsion #1		
	% Moisture	Retention		% Moisture	Retention		% Moisture	Retention	
		p.p.m.	%		p.p.m.	%		p.p.m.	%
Before mashing	79.3	483	100.00	78.0	454	100.00	78.6	2,370	100.00
After predrying	43.3	13±3	2.69	29.8	11±0	2.42	42.0	228±147	9.62
After granulation	19.5	10±0.8	2.07	22.1	7±0.4	1.54	18.0	80±0	3.38
After drying	7.4	5±0.4	1.04	10.7	0	0	12.55	61±31	2.57

Antioxidant concentration was calculated on a dry matter basis.

Table 3. Effect of processing temperature in the F-T process on retention of BHT when applied as emulsion #1 at the mashing step.

Processing step	I (85°C)			II (60°C)			III (50°C)		
	% Moisture	Retention		% Moisture	Retention		% Moisture	Retention	
		p.p.m.	%		p.p.m.	%		p.p.m.	%
Before mashing	73.5	1,887	100.00	76.5	426	100.00	76.3	422	100.00
After predrying	30.7	208±2	11.02	36.5	0	0	33.9	18±1	4.27
After granulation	13.1	116±47	8.79	29.1	0	0	13.6	14±0	3.32
After drying	10.9	107±0	5.67	9.5	0	0	10.2	7±0.3	1.66

I. Control (normal predrying and drying temperature of 85°C

II. Predrying and drying temperatures of 60°C

III. Predrying and drying temperatures of 50°C

Antioxidant concentration was calculated on a dry matter basis

the antioxidant. These results agree well with those of Kirleis and Stine (1978) that BHT and BHA were completely lost from a gelatinized starch-antioxidant model system when the freeze-drying time was doubled.

The volatility of the antioxidants was increased further when they were applied as an ethanol spray (Table 4). When the spray was applied during the mashing step, less than 1% of BHT was retained in the final product. In an attempt to improve the retention, the spray was applied on the thawed mashed potatoes in one experiment, while in another experiment half was applied during mashing and the rest during thawing. In both cases no BHT was found in the final product. It appeared that a significant amount of the antioxidant was lost during spraying through the loss of the highly volatile fine mist. Furthermore, ethanol lowered the vapor pressure above the product during the heating process, thus substantially increasing the volatility of the antioxidant. Even when this technique was applied to explosion puffed potatoes, using N_2 as the atomizing agent (Konstance et al., 1978), the loss of antioxidant was found to be so great that its initial concentration would have to be at least five times greater than the concentration required in the final product.

From our experiments it was evident that the loss

Table 4. Retention of BHT when applied in an ethanol spray (approx. 4% solution) at different steps of the F-T process.

Processing step	I			II			III		
	% Moisture	Retention		% Moisture	Retention		% Moisture	Retention	
		p.p.m.	%		p.p.m.	%		p.p.m.	%
Before mashing	78.0	2,237	100.00	78.0	455	100.00	77.0	435	100.00
After predrying	37.8	13±0	0.57	36.0	0	0	25.4	4±0	0.92
After granulation	28.3	11±7	0.48	17.8	0	0	9.9	4±0	0.92
After drying	8.4	7±0.6	0.31	8.7	0	0	8.6	0	0

I. Applied during mashing

II. Applied during thawing

III. 50% applied during mashing and 50% during thawing

Antioxidant concentration was calculated on a dry matter basis

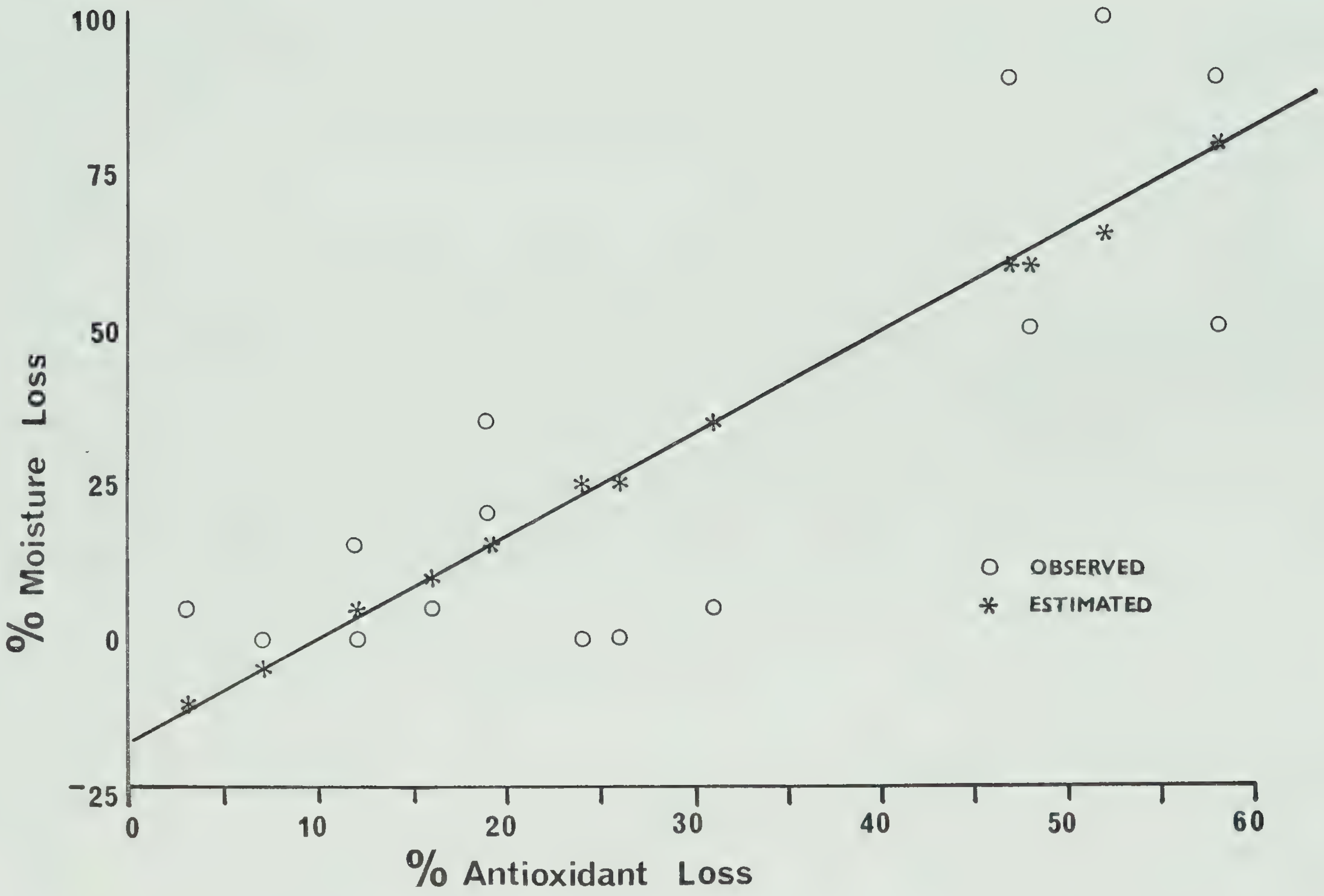

Figure **8** Effect of moisture loss on retention of antioxidants in freeze-thaw potato granules.

Table 5. Correlation coefficients (r) and slopes (b) of regression lines from the plots of per cent antioxidant loss vs per cent moisture loss during the F-T process.

Mode of antioxidant application	r	b
Powder	0.85*	0.80
Emulsion	0.89*	1.82
Ethanol spray	0.92*	1.90

* Significant at $p = 0.05$

Total $r = 0.82$ Df = 14

of antioxidants was associated with the loss of moisture from the product during the process. To substantiate this hypothesis, the percent loss of antioxidants, applied as powder, emulsion or ethanol spray, was plotted against the corresponding percent loss of moisture during various steps of the F-T process (Fig. 8). When simple correlation and regression analysis was applied to the results, the r-values and the slopes of the regression lines obtained were as shown in Table 5. All r-values were significant at $p = 0.05$, indicating a strong relationship between the loss of antioxidant and the loss of moisture through evaporation. Kirleis and Stine (1978) made a similar observation when they found a strong relationship between BHA retention and the moisture content of the product. They found that products with higher moisture contents retained greater amounts of BHA than those with lower moisture contents.

Steam distillation and volatilization of antioxidants are the two major mechanisms responsible for antioxidant loss. The loss is variable and is dependent on the method of antioxidant application, as indicated by the slopes (b) of the regression lines. The slope of the line of antioxidant addition in the form of a powder was the lowest (0.80), indicating that in this case the least antioxidant was lost per unit of moisture loss. About

0.80% of the antioxidants was lost for each 1% moisture evaporated. The highest antioxidant loss per 1% moisture removal was found when the antioxidant was applied as an ethanol spray (b = 1.90), and the next highest loss was when it was applied as an emulsion (b = 1.82) (Fig. 4) (Table 5).

This is as expected, since ethanol accentuates the steam distillation and volatilization of the antioxidants during the heating process by its ability to lower the vapor pressure above the product. A similar effect, though to a slightly lesser degree, occurred when the antioxidant was dispersed in the surfactant emulsion prior to addition to mashed potatoes.

The levels of antioxidants in food products are subject to regulation. In the fifteenth report of the joint FAO/WHO Expert Committee on Food Additives a combination of antioxidants at a level of 0.001% (10 ppm) on a wet weight basis was reported to be used commonly in the dehydrated potato granule industry (FAO, 1972). The legal status in Canada for phenolic antioxidants in dehydrated potatoes is 0.005% (50 ppm) for BHA or BHT alone, or for a mixture of the two with or without PG (Hadziyev and Steele, 1979).

In commercial potato granule production with the A-B process, the recovery of antioxidant is only about

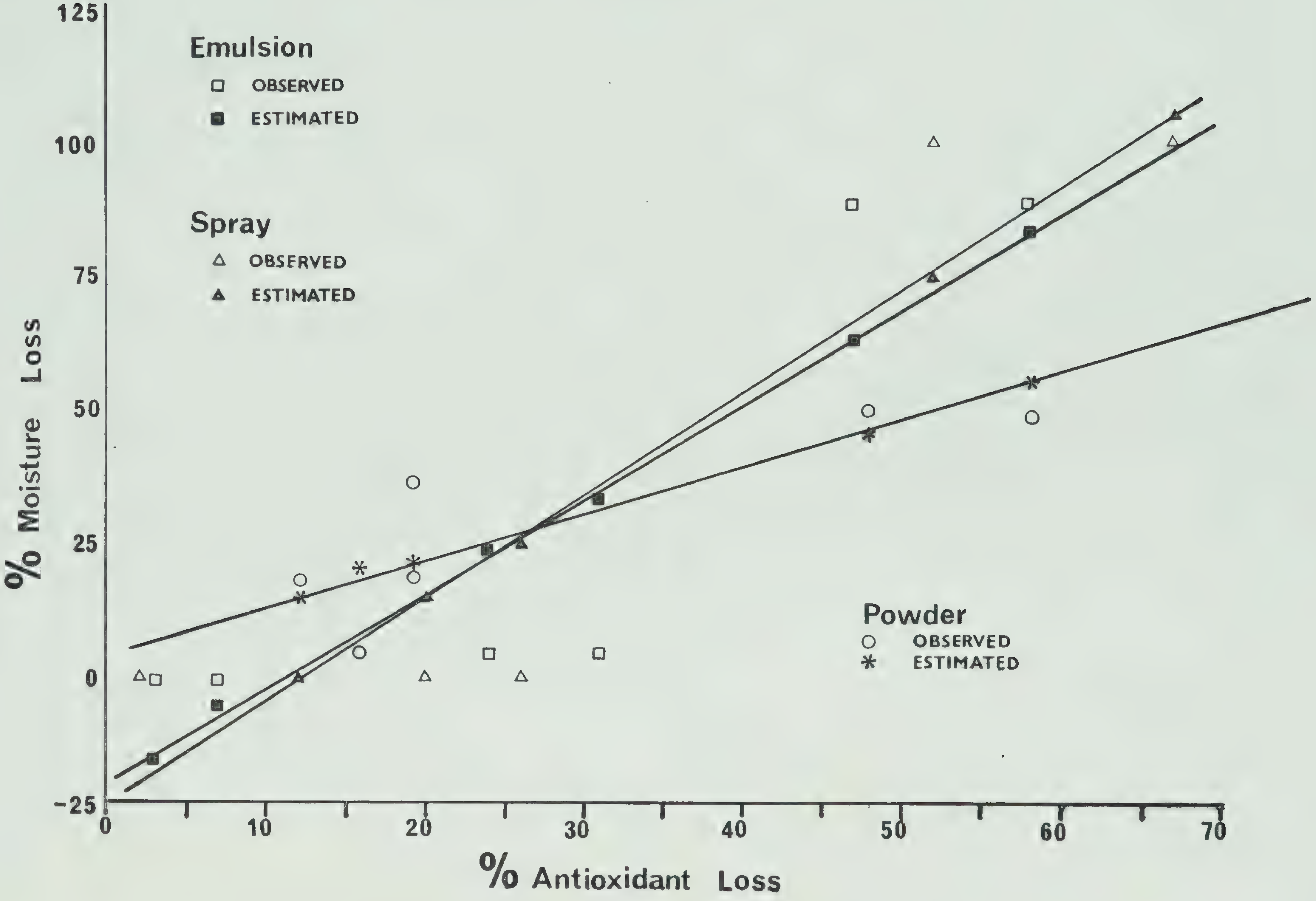

Figure **9** Effect of modes of antioxidant application.

10% due to the typical losses incurred mostly from volatilization and steam distillation during addition of antioxidants to the hot mash and during drying of the mash. From the results of this study, in order to obtain 50 ppm antioxidant in the F-T process end-product, at least 500 ppm (dry weight basis) should be applied during mashing in the form of a powder, with surfactants also being added at this stage.

8.3 Storage Test

The retention pattern of BHT and BHA, applied by three methods, in F-T potato granules packaged in polyethylene bags and stored at 25°C and 37°C for 6 weeks is shown in Table 6. The per cent retention, based on the initial quantities of the antioxidants in the granules, is also plotted against storage time (Fig. 10). Unfortunately, the initial quantity of antioxidants could not be standarized for all cases due to difficulties in processing, the inherent characteristics of the application methods, and time limitations of the project. Nevertheless, the overall picture can be delineated as follows. Firstly, there was no significant difference between the two storage temperatures with respect to the retention of the antioxidants. Secondly, antioxidants applied in powder form had a better retention during storage.

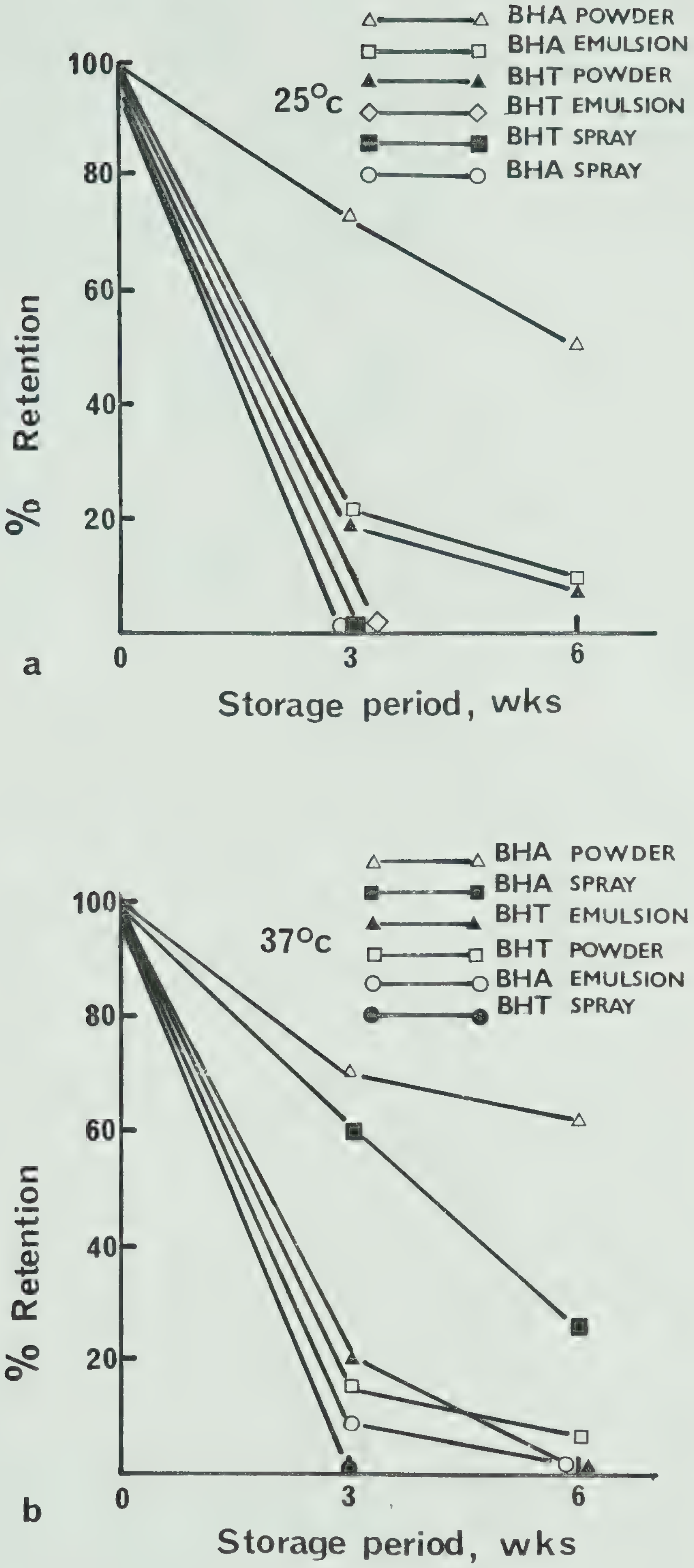

Figure **10** Effect of storage on retention of BHT and BHA in potato granules packaged in polyethylene bags.

Table 6. Effect of storage at 25°C and 37°C on retention of BHT and BHA in potato granules packaged in polyethylene bags.

Treatment	Moisture %	25°C			37°C		
		p.p.m. retained			p.p.m. retained		
		0 week	3 weeks	6 weeks	0 week	3 weeks	6 weeks
Applied as powder:							
BHT	8.5	303±43	60±11	23±4	303±43	44±9	21±0
BHA	13.6	89±10	65± 5	49±4	89±10	62±5	54±0
Applied as emulsion:							
BHT	12.5	20± 3	0	0	20± 3	4±0.7	0
BHA	12.7	122± 8	26± 5	10±2	122± 8	18±0	2±0
Applied as ethanol spray:							
BHT	9.4	15± 6	0	0	15± 6	0	0
BHA	9.4	8± 2	0	0	8± 2	5±2	2±2

Antioxidant concentration was calculated on a dry matter basis.

Thirdly, in all cases BHA had a better retention than BHT. This is particularly interesting, because the results in the previous section showed that BHT was retained to a greater degree than BHA over the process. Yet, during storage the reverse was true. This may indicate that BHT can withstand heat processes better than BHA, but it is lost at a greater rate than BHA through oxidization or interaction with potato constituents during storage. The storage results, thus, appear to confirm the observations made by Kirleis and Stine (1978) that there is a greater retention of BHA than BHT in freeze-dried, starch-based model systems. Finally, the results of the present study show that BHT applied in an emulsion or ethanol spray was completely lost after 3 to 6 weeks of storage at either 25°C or 37°C. BHA seems to be retained slightly better than BHT for both of the application techniques. These results indicate that the powder application technique is the most suitable mode for the F-T granule process.

Stuckey (1975) showed that BHA is more stable than BHT in low-fat products. He stated that a dehydrated wheat-based product processed with 50 ppm BHA took approximately 3 more days to develop rancidity at 63°C than when processed with an equal amount of BHT. This point is illustrated clearly when per cent antioxidant retention

is plotted against storage time (Figures 10a and 10b). At both 25 and 37°C storage temperatures about 55-60% of BHA, applied as powder, was retained after 6 weeks while only about 8% of BHT was retained. It may be concluded, therefore, that in regards to storage stability BHA is more effective than BHT for F-T potato granules. However, if process stability of antioxidants is taken into account, a combination of BHA and BHT at a suitable ratio may prove to be most effective. This was demonstrated to be so by Stuckey (1975), who showed that a combination of 10 ppm each of BHA and BHT, instead of 50 ppm of just one of the antioxidants, could double the shelf life of a dehydrated cereal product.

It is not clear from storage experiments why antioxidant applied as emulsion or ethanol spray was much less stable than when applied as powder. The answer may lie in the way in which the antioxidant is dispersed in the product - whether it is uniformly distributed or only associated with some constituents (cellulose, lipid, pectin, starch) of the product. Also, the location in the product, that is, within or on the external surface of the single cell of a granule, and the form in which the antioxidant exists (i.e., as crystals, as a solute in the lipid phase, or distributed on cellulose pectin or starch matrices) will partly determine its stability

and effectiveness. Further study is required to elucidate these questions.

9. CONCLUSION

The pulse polarographic method for the analysis of BHT and BHA has proved satisfactory. No interference from α-tocopherol or β-carotene, both found in potatoes, was experienced. Sensitivity was good to as low as 2 ppm, and reproducibility was quite acceptable.

Application of antioxidants in powder form, together with surfactants, during mashing was found to give the highest antioxidant retention in potato granules produced with the F-T process. BHT was more stable during the process than BHA. The loss of the antioxidants was proportional to the loss of moisture during the process, indicating steam distillation as the major factor causing the loss. Lowering processing temperatures did not reduce the loss, as a longer processing time was required to remove the same quantity of moisture. Applying antioxidants in an emulsion or ethanol solution resulted in poorer retention. This was attributed to the increased volatility of the antioxidants in the emulsion or ethanol solution.

No significant difference was detected in antioxidant stability when potato granules were stored either at 25°C or 37°C. Antioxidants added in powder form during the process were retained better during the 6 weeks of

storage than those added in an emulsion or ethanol solution. In all cases BHA was more stable during storage than BHT. About 60% of BHA was retained after 6 weeks of storage when it was added as powder.

To obtain 50 ppm antioxidant in the potato granule end-product and for the highest retention and stability during processing and storage, a combination of BHT and BHA at a combined concentration of 500 ppm on a dry matter basis is suggested. It should be added in powder form, along with an appropriate quantity of surfactants, during the mashing step of the F-T granule process.

10. RECOMMENDATIONS FOR FURTHER WORK

The present study showed that during an F-T dehydrated potato granule process the losses of antioxidant are closely related to the loss of moisture by steam distillation in the different processing steps. The distribution and retention status of antioxidants in the final product is not clear. Also, to be clarified are the antioxidant locations in potato granules (on the surface, within the granule cell, in cell wall, in the lipid layer surrounding the gelatinized and retrograded starch matrix, or entrapped within the starch matrix).

The surface effect on phenol retention, the possible involvement of hydrogen bonds, and protein-phenol interaction and/or effect of matrix charge should also be clarified. The antioxidants may be added as ethanol solution to study such effects, or as "micelles" in a formulation with monoglyceride emulsifier to discover if the retention can be enhanced via "micelles", or via clathrate compound formation, with starch helices as the host compound.

Possible new methods of antioxidant incorporation into granules to improve retention of the antioxidants

in the F-T process should be found to obtain an appropriate concentration in the final product. A comparative study between the A-B and F-T processes with respect to antioxidant retention at various processing steps is also recommended.

The differential pulse voltammetry method for the analysis of antioxidants has proved to be satisfactory in the present work. However, in order to assess its convenience in a processing quality control laboratory, comparisons with other techniques such as spectrofluorometry, gas-liquid chromatography, thin-layer-rod chromatography (combined with a flame ionization detector system) and colorimetry should be made in order to find a fast and economical method suitable for quality control purposes. Special attention should be given to fluorometry and thin-layer-rod chromatography, since both appear to provide a sensitivity better than 0.01 ppm for quantitation of BHA and/or BHA + BHT.

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B30287